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SUPPORTING INFORMATION

Cu-Catalyzed Enantioselective Allyl–Allyl Cross Coupling

*Valentín Hornillos, Manuel Pérez, Martín Fañanas-Mastral and Ben L. Feringa**

Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands.

1. General Procedures:

Chromatography: Merck silica gel type 9385 230-400 mesh, TLC: Merck silica gel 60, 0.25 mm. Components were visualized by UV and potassium permanganate staining. Progress and conversion of the reaction were determined by GC-MS (GC, HP6890: MS HP5973) with an HP1 or HP5 column (Agilent Technologies, Palo Alto, CA). Mass spectra were recorded on an AEI-MS-902 mass spectrometer (EI+) or a LTQ Orbitrap XL (ESI+). ^{1}H- and ^{13}C-NMR were recorded on a Varian AMX400 (400 and 100.59 MHz, respectively) or a Varian VXR300 (300 and 75 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ 7.26 for ^{1}H, δ 77.0 for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Enantiomeric ratios were determined by HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector or by capillary GC analysis (HP 6890, CP-Chiralsil-Dex-CB column (25 m x 0.25 mm) using flame ionization detector.

All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. Dichloromethane was dried and distilled over calcium hydride; THF was dried and distilled over sodium. All copper-salts (CuTC, $CuBr{\bullet}SMe_2$, CuI, CuCl, $Cu(OTf)_2$, CuCN, $(CuOTf)_2{\bullet}Tol$, $Cu(MeCN)_4PF_6$ and $(CuOTf)_2{\bullet}C_6H_6$) were purchased from Aldrich, and used without further purification. Allyl bromides **1a**,[1] **1c**,[2] **1f**,[1] **1i**,[3] **1j**,[3] **1k**,[3] **1l**[4] and **1m**,[4] **1n**, [5] **1o**,[6] were prepared following a literature procedure**.** AllylMgBr (1.0 M in Et_2O), AllylMgCl (1.0 M in THF), Tetraallyltin, Hoveyda-Grubbs Catalyst 2nd Generation (HG-II), Ligands (*R,R*)-Taniaphos (**L1**) and *Tol*-BINAP (**L10**) were purchased from Aldrich. AllylLi was

[1] Hornillos, V., van Zijl, A.W., Feringa, B.L., *Chem. Comm.* **2012**, *48(31)*, 3712-3714.
[2] Armstrong, A. Gethin, D.M., Wheelhouse, C.J. *Synlett*, **2004**, *2*, 350-352.
[3] Teichert, J.T., Zhang, S., van Zijl, A.W., Slaa, J.W., Minnaard, A.J., Feringa, B.L., *Org. Lett.*, **2010**, *12(20)*, 4658-4660.
[4] Vyas, D.J., Oestreich, M., *Chem. Comm.*, **2010**, *46(4)*, 568-570.
[5] Ellwood, A.R., Mortimer, A.J.P., Tocher, D.A., Porter, M.J., *Synlett*, **2008**, *14*, 2199-2203.
[6] Camps, F., Gasol, V., Guerrero, A., *Synthesis*, **1987**, *5*, 511-12.

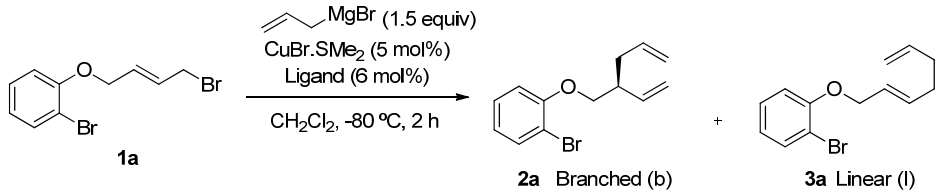
prepared as reported in the literature.[7] Phosphoramidite ligands **L6** and **L9** were purchased from Strem Chemicals. Phosphoramidite ligands (**L2**, **L3),**[8] (**L4**, **L5),**[9] **L7**,[10] and **L11**[11] and those used in **Table S1**[10] were prepared as reported in the literature. Phosphoramidite ligand (*S*,*R*,*R*)-**L7** was prepared following the same procedure described for (*S*,*S*,*S*)-**L7**.[12]

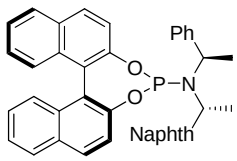
Enantiomeric ratios were measured by preparation of both enantiomers of each product.

[7] Dunne, K. S.; Lee, S. E.; Gouverneur, V. *J. Organomet. Chem*. **2006**, *691*, 5246–5259.
[8] Tissot-Croset, K.; Polet, D.; Gille, S.; Hawner, C.; Alexakis, A. *Synthesis* **2004**, 2586–2590.
[9] Feringa, B. L.; Pineschi, M.; Arnold, L. A.; Imbos, R.; De Vries, A. H. M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2620–2623.
[10] Teichert, J. F.; Feringa, B. L. *Angew. Chem. Int. Ed*. **2010**, *49*, 2486.
[11] Choi, Y. H.; Choi, J. Y.; Yang, H. Y.; Kim, Y. H. *Tetrahedron: Asymmetry* **2002**, *13*, 801-804.
[12] Alonso, I.; Trillo, B.; López, F.; Montserrat, S.; Ujaque, G.; Castedo, L.; Lledós, A.; Mascareñas, J. L. *J. Am. Chem. Soc*. **2009**, *131*, 13020–13030.

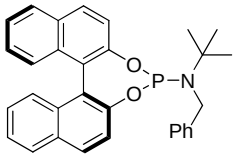
2. Screening results and additional information

Table S1. Additional phosphoramidites ligands screened for the copper-catalyzed enantioselective Allyl-Allyl cross coupling.

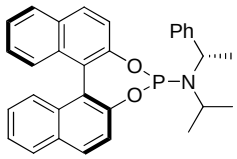




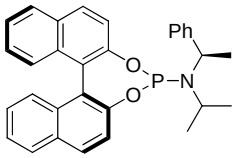
(**b**:**l**) 45:55, 95:5 e.r.



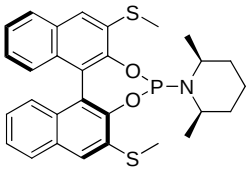
(**b**:**l**) 48:52, 93:7 e.r.



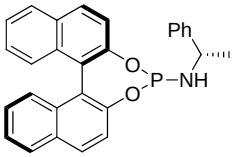
(**b**:**l**) 29:71, 64:36 e.r.



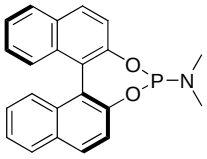
(**b**:**l**) 52:48, 92:8 e.r.



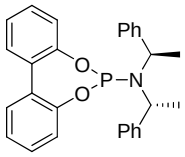
(**b**:**l**) 35:63, 50:50 e.r.



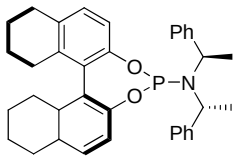
(**b**:**l**) 29:71, 50:50 e.r.



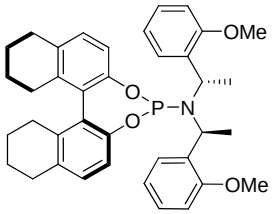
(**b**:**l**) 12:88, 62:38 e.r.



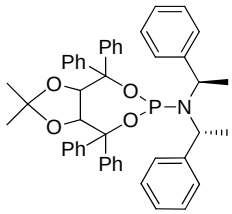
(**b**:**l**) 60:40, 95:5 e.r.



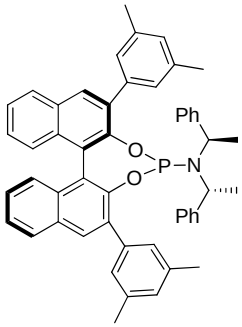
(**b**:**l**) 65:35, 95:5 e.r.



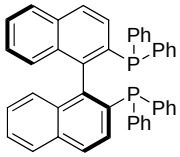
(**b**:**l**) 51:49, 95:5 e.r.



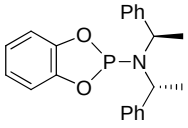
(**b**:**l**) 21:79, 59:41 e.r.



(**b**:**l**) 52:48, 74:26 e.r.



(**b**:**l**) 45:55, 74:26 e.r.



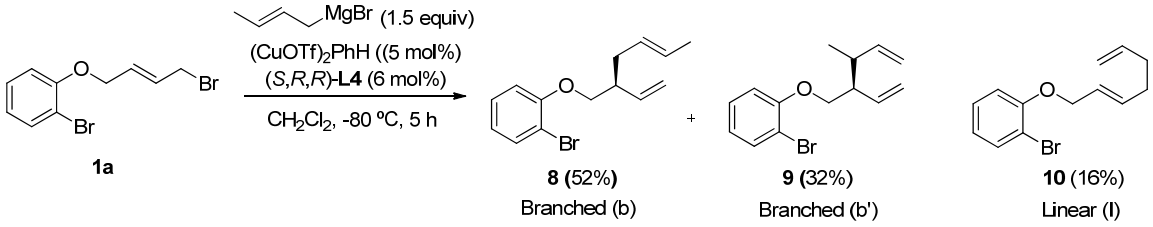
(**b**:**l**) 48:52, 93:7 e.r.

Table S2. Effect of different conditions and influence of copper source on the reaction

entry[a]	Other conditions	[Cu] source	**2a**:**3a**[c]	**2a**, e.r.[d]
1	Cu/L 1:2	$CuBr \bullet SMe_2$	66:34	96:4
2	Reaction carried out at -74 °C	$CuBr \bullet SMe_2$	64:36	95:5
3	Reaction carried out in TBME[e]	$CuBr \bullet SMe_2$	24:76	63:37
4	Reaction carried out in Toluene	$CuBr \bullet SMe_2$	54:46	60:40
5		CuI	68:32	97:3
6		CuCl	67:33	97:3
7		$Cu(OTf)_2$	56:44	97:3
8		$(CuOTf)_2 \bullet Tol$	75:25	97:3
9		$Cu(MeCN)_4PF_6$	74:26	97:3

[a]Conditions: 0.2 mmol of allyl bromide, 1.5 eq of allyl magnesium bromide diluted in CH_2Cl_2, 0.05 M in CH_2Cl_2, The substrate was added over 5 h. [b]Conversion by GC-MS. All reaction gave full conversion unless noted. [c]branched/linear ratios determined by GC-MS or ^1H NMR spectroscopy. [d]Determined by chiral HPLC analysis. [e]TBME= Methyl *tert*-butyl ether.

By raising the ligand/copper ratio from 1:1 to 2:1 the regioselectivity slightly decreased (b,l=66:34) although the e.r. ratio was maintained (entry 1). Upon raising the temperature to -74 ºC (entry 2), conversion of the σ-complex to the π-complex can occur,[13] resulting in a lower regioselectivity. The choice of dichloromethane as the solvent is key to obtain high regio- and enantioselectivity. The use of toluene or ethereal solvents as TBME caused a drastic drop in both regio- and enantioselectivity (entries 3 and 4).

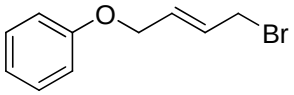


Scheme S1. Cu-catalyzed reaction between **1a** and crotylmagnesium bromide

[13] Bartholomew, E. R.; Bertz, S. H.; Cope, S.; Murphy, M.C.; Ogle. A. *J. Am. Chem. Soc*. **2008,** 130, 11244–11245.

3. Synthesis of allylic bromides:

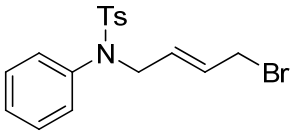
(E)-(4-bromobut-2-enyloxy)benzene (2a)



The same procedure as for **1a** was followed.[1] [87% yield]

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.29 (m, 2H), 6.97 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.05 (m, 2H), 4.56 (dd, *J* = 0.9, 4.7 Hz, 2H), 3.99 (dd, *J* = 0.5, 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 158.3, 130.1, 129.5 (2C), 129.2, 121.0, 114.6 (2C), 7.1, 31.6. EI-MS m/z (%) 226 (18), 147 (100).

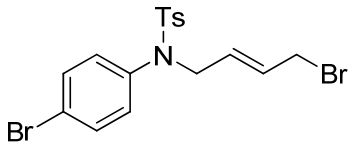
(E)-*N*-(4-bromobut-2-enyl)-4-methyl-*N*-phenylbenzenesulfonamide (4a)



The same procedure as for **6a** was followed.[1] [72% yield]

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.48 (d, *J* = 8.3 Hz, 2H), 7.27 (m, 5H), 7.02 (m, 2H), 5.70 (m, 2H), 4.18 (d, *J* = 5.0 Hz, 2H), 3.80 (d, *J* = 6.5 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.5, 139.0, 135.3, 130.4, 129.6, 129.5 (2C), 128.9 (2C), 128.8 (2C), 127.9, 127.7 (2C), 52.0, 31.3, 21.6.

(E)-*N*-(4-bromobut-2-enyl)-*N*-(4-bromophenyl)-4-methylbenzenesulfonamide (5a)

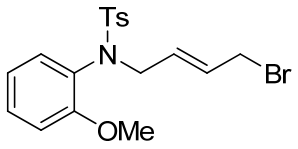


The same procedure as for **6a** was followed.[1] [67% yield]

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.47 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 2H), 5.68 (m, 2H), 4.14 (d, *J* = 6.0 Hz, 2H), 3.79

(d, J = 6.7 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.9, 138.0, 134.9, 132.2 (2C), 130.8, 130.4 (2C), 129.6 (2C), 129.2, 127.7 (2C), 121.9, 51.9, 31.9, 21.6.

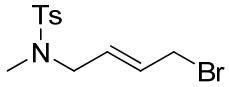
***(E)*-*N*-(4-bromobut-2-enyl)-*N*-(2-methoxyphenyl)-4-methylbenzenesulfonamide (7a)**



The same procedure as for **6a** was followed.[1] [77% yield]

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.55 (d, J = 8.5 Hz, 2H), 7.25 (m, 4H), 6.91 (t, J = 7.3 Hz, 1H), 6.76 (d, J = 8.5 Hz, 1H), 5.71 (m, 2H), 4.19 (bs, 2H), 3.81 (d, J = 6.0 Hz, 2H), 3.40 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 156.3, 142.8, 137.3, 133.2, 130.6, 129.8, 129.6, 129.0 (2C), 127.6 (2C), 126.5, 120.6, 111.5, 54.9, 51.1, 31.7, 21.5.

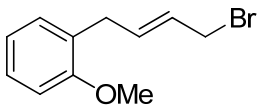
***(E)*-*N*-(4-bromobut-2-enyl)-*N*-methyl-4-methylbenzenesulfonamide (8a)**



The same procedure as for **6a** was followed.[1] [68% yield]

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.66 (d, J = 8.1 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 5.84 (m, 1H), 5.66 (m, 1H), 3.89 (d, J = 7.2 Hz, 2H), 3.64 (d, J = 6.5 Hz, 2H), 2.66 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.5, 134.3, 130.7, 129.7 (2C), 129.4, 127.5 (2C), 51.3, 34.4, 31.2, 21.5.

***(E)*-1-(4-bromobut-2-enyl)-2-methoxybenzene (15a)**



To a solution of 1-allyl-2-methoxybenzene (2.5 mmol, 374 mg) and 1,4-dibromobutene (12.6 mmol, 2.7 g) in dry toluene (20 mL), HG-II catalyst (0.25 mmol, 157 mg) was added and the mixture was heated at 80 °C for 10h. The mixture was cooled down to

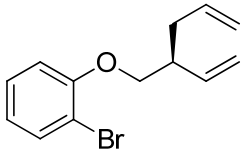
room temperature and the solvent was removed under reduced pressure to yield the crude product which was purified by flash chromatography on silica gel, *n*-pentane/Et_2O 98:2. [67% yield].^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.81 (dt, *J* = 1.6, 7.5 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.51 (dt, *J* = 0.9, 7.5 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 6.55 (m, 1H), 6.34 (m, 1H), 4.56 (d, *J* = 7.4 Hz, 2H), 4.43 (s, 3H), 3.99 (d, *J* = 7.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 157.2, 134.5, 129.8, 127.8. 127.6, 127.1, 120.5, 110.4, 55.3, 33.4, 32.7.

4. General procedure for the copper-catalyzed enantioselective allyl-allyl cross coupling:

A Schlenk tube equipped with septum and stirring bar was charged with $(CuOTf)_2$•C_6H_6 (0.01 mmol, 5 mol%, 2.60 mg) and the appropriate phosphoramidite ligand (0.011 mmol, 5.5 mol%). Dry dichloromethane (2 mL) was added and the solution was stirred under nitrogen atmosphere at room temperature for 20 min and the resulting solution was cooled to -80 °C. Then, the corresponding allyl bromide **1** (0.2 mmol) in dichloromethane (1 mL) was added. In a separate Schlenk flask, allylMgBr (1.0 M in Et_2O, 0.30 mmol, 300μL, 1.5 eq) was diluted with dichloromethane (combined volume of 1 mL) under nitrogen and added dropwise to the reaction mixture over 5 h using a syringe pump. Once the addition was complete, the mixture was stirred at -80 °C for 16 h. The reaction was quenched with MeOH (1 mL), saturated aqueous NH_4Cl solution (2 mL) and the mixture was warmed up to room temperature, diluted with dichloromethane and the layers were separated. The aqueous layer was extracted with dichloromethane (3 x 5 mL) and the combined organic layers were dried with anhydrous Na_2SO_4, filtered and the solvent was evaporated *in vacuo*. The crude product was purified by flash chromatography on silica gel using different mixtures of *n*-pentane/EtOAc or *n*-pentane/Et_2O as the eluent.

Note: GC-MS or ^{1}H-NMR analysis was carried out to determine the b:l ratio on a sample obtained after aqueous extraction with dichloromethane.

5. Compound characterization:

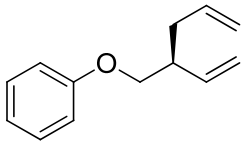


(-)-(2-Bromo-2-(2-vinylpent-4-enyloxy)benzene) (2a): The title compound was prepared from **1a** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 1:99, R_f = 0.7) afforded **2a** (71% yield, 77:23 ratio (b:l), 97:3 e.r.) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.53 (dd, *J* = 1.5, 7.9 Hz, 1H), 7.24 (m, 1H), 6.84 (m, 2H), 5.84 (m, 2H), 5.12 (m, 4H), 3.96 (m, 2H), 2.68 (m, 1H), 2.48 (m, 1H), 2.31 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 155.2, 138.4, 135.9, 133.3, 128.3, 121.8, 116.7, 116.3, 113.2, 112.3, 71.3, 43.0, 35.5.

$[\alpha]_D^{20}$ = -17.6 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{13}H_{15}BrO$, $[M+H^+]$: 267.0385; found: 267.0379.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 99.8:0.2, 40 °C, 210 nm, retention times (min): 16.4 (minor) and 16.7 (major).

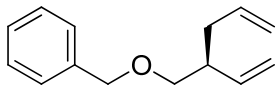


(+)-(2-Vinylpent-4-enyloxy)benzene (2b). The title compound was prepared from **1b** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 1:99, R_f = 0.7) afforded **2b/3b** (89% yield, 70:30 ratio (b:l), 95:5 e.r.) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.28 (m, 2H), 6.93 (m, 3H), 5.80 (m, 2H), 5.08 (m, 4H), 3.92 (d, *J* = 6.2 Hz, 2H), 2.63 (m, 1H), 2.41 (m, 1H), 2.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 158.9, 138.7, 136.0, 129.4 (2C), 120.6, 116.6, 116.1, 114.6 (2C), 70.3, 43.0, 35.7.

$[\alpha]_D^{20}$ = +14 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{13}H_{17}O$, $[M+H^+]$: 189.1279; found: 189.1274.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OD-H column, *n*-heptane/*i*-PrOH 100:0, 40 °C, 206 nm, retention times (min): 13.6 (major) and 15.4 (minor).

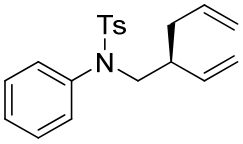


(+)-((2-Vinylpent-4-enyloxy)methyl)benzene (2c). The title compound was prepared from **1c** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 1:99, R_f = 0.8) afforded **2c** (76% yield, 82:18 ratio (b:l), 95:5 e.r.) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.34 (m, 5H), 5.76 (m, 2H), 5.06 (m, 4H), 4.52 (s, 2H), 3.43 (d, *J* = 6.3 Hz, 2H), 2.46 (m, 1H), 2.31 (m, 1H), 2.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 139.5, 138.5, 136.4, 128.3 (2C), 127.5 (2C), 127.4, 116.1, 115.6, 73.0, 73.0, 43.5, 35.8.

$[\alpha]_D^{20}$ = +48 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{14}H_{19}O$, $[M+H^+]$: 203.1436; found: 203.1430.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OB-H column, *n*-heptane/*i*-PrOH 100:0, 40 °C, 204 nm, retention times (min): 15.4 (major) and 16.1 (minor).

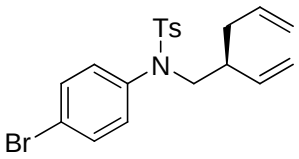


(-)-4-Methyl-*N*-phenyl-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2d): The title compound was prepared from **1d** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.7) afforded **2d/3d** (90% yield, 83:17 ratio (b:l), 96:4 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.43 (d, *J* = 8.3 Hz, 2H), 7.29 (m, 3H), 7.22 (d, *J* = 7.8 Hz, 2H), 7.03 (m, 2H), 5.63 (m, 2H), 5.07-4.90 (m, 4H), 3.48 (m, 2H), 2.41 (s, 3H), 2.26 (m, 1H), 2.15 (m, 1H), 2.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.3, 139.2, 138.9, 135.6, 135.1, 129.3 (2C), 128.9 (2C), 128.8 (2C), 127.8, 127.7 (2C), 116.6, 116.5, 54.0, 41.9, 36.3, 21.5.

$[\alpha]_D^{20}$ = -17 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{20}H_{24}NO_2S$, $[M+H^+]$: 342.1528; found: 342.1522.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 247 nm, retention times (min): 38.5 (major) and 40.0 (minor).

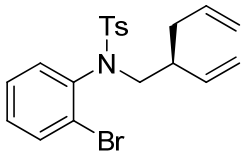


(-)-*N*-(4-bromophenyl)-4-methyl-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2e): The title compound was prepared from **1e** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.7) afforded **2e/3e** (88% yield, 82:18 ratio (b:l), 97:3 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.42 (d, *J* = 8.3 Hz, 4H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.90 (d, *J* = 9.1 Hz, 2H), 5.61 (m, 2H), 5.08-4.89 (m, 4H), 3.44 (m, 2H), 2.42 (s, 3H), 2.21 (m, 1H), 2.09 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.6, 138.7, 138.3, 135.4, 134.7, 132.1 (2C), 130.4 (2C), 129.5 (2C), 127.6 (2C), 121.6, 116.8, 116.7, 53.8, 41.9, 36.3, 21.5.

$[\alpha]_D^{20}$ = -14 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{20}H_{23}BrNO_2S$, $[M+H^+]$: 420.0633; found: 420.0627.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 250 nm, retention times (min): 49.8 (minor) and 51.6 (major).



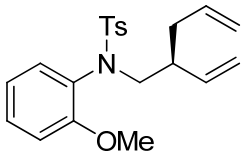
(-)-*N*-(2-bromophenyl)-4-methyl-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2f): The title compound was prepared from **1f** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.7) afforded **2f/3f** (90% yield, 90:10 ratio (b:l), 94:6 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.56 (m, 3H), 7.26 (m, 5H), 5.60 (m, 2H), 4.96 (m, 4H), 3.68 (m, 1H), 3.49 (m, 1H), 2.42 (s, 3H), 2.44-2.20 (m, 1H), 2.16-1.93 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.5, 139.1, 138.3, 137.9, 136.5, 136.4, 135.8, 135.7, 134.1, 134.0, 133.5, 132.3, 129.7, 129.5, 129.4,

129.4, 128.0, 127.9, 127.8, 127.7, 116.6, 116.5, 116.4, 55.0, 54.6, 42.9, 42.9, 42.3, 39.6, 36.6, 21.6.

$[\alpha]_D^{20}$ = -23 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{20}H_{23}BrNO_2S$, $[M+H^+]$: 420.0633; found: 420.0627.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 246 nm, retention times (min): 41.8 (minor) and 43.5 (major).

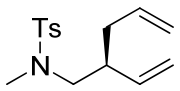


(+)-*N*-(2-Methoxyphenyl)-4-methyl-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2g): The title compound was prepared from **1g** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.6) afforded **2g/3g** (87% yield, 91:9 ratio (b:l), 97:3 e.r.) as a waxy solid. ^1H NMR (400 MHz, $CDCl_3$), δ: 7.50 (d, *J* = 8.1 Hz, 2H), 7.31-7.17 (m, 4H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 5.63 (m, 2H), 5.07-4.84 (m, 4H), 3.58 (m, 2H), 3.32 (s, 3H), 2.39 (s, 3H), 2.32 (m, 1H), 2.18 (m, 1H), 2.04 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 142.6, 139.5, 137.3, 136.1, 133.6, 129.6, 128.9, 128.8 (2C), 127.6 (2C), 126.7, 120.5, 116.2, 116.1, 111.5, 54.7, 53.4, 42.8, 36.3, 21.4.

$[\alpha]_D^{20}$ = +20 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{21}H_{26}NO_3S$, $[M+H^+]$: 372.1633; found: 372.1628.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AS-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 228 nm, retention times (min): 29.8 (minor) and 31.7 (major).



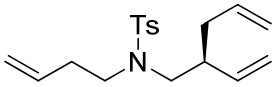
(+)-*N*-Methyl-4-methyl-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2h): The title compound was prepared from **1h** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.7) afforded **2h/3h** (81% yield, 74:26

ratio (b:l), 96:4 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.65 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 7.7 Hz, 2H), 5.75 (m, 1H), 5.61 (m, 1H), 5.02 (m, 4H), 3.01 (dd, J = 7.3, 13.2 Hz, 1H), 2.83 (dd, J = 7.7, 13.2 Hz, 1H), 2.69 (s, 3H), 2.42 (s, 3H), 2.39 (m, 1H), 2.26 (m, 1H), 2.08 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.2 (2C), 139.0, 135.8, 129.6 (2C), 127.4 (2C), 116.6, 116.5, 54.1, 42.1, 36.4, 35.4, 21.5.

$[\alpha]_D^{20}$ = +5.2 (c = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{15}H_{22}NO_2S$, $[M+H^+]$: 280.1371; found: 280.1366.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 228 nm, retention times (min): 36.2 (major) and 38.9 (minor).

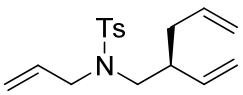


(+)-*N*-(But-3-enyl)-4-methyl-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2i): The title compound was prepared from **1i** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.8) afforded **2i/3i** (93% yield, 75:25 ratio (b:l), 96:4 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.68 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.72 (m, 2H), 5.58 (m, 1H), 5.02 (m, 6H), 3.15 (m, 3H), 3.00 (m, 1H), 2.42 (s, 3H), 2.42 (m, 1H), 2.25 (m, 3H), 2.04 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.1, 139.2, 136.9, 135.8, 134.7, 129.6 (2C), 127.2 (2C), 116.9, 116.7, 116.5, 52.3, 48.2, 42.6, 36.5, 32.8, 21.5.

$[\alpha]_D^{20}$ = +12 (c = 1.0, $CHCl_3$).

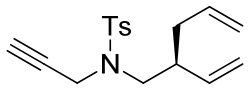
HRMS (ESI+, *m/z*): calcd. for $C_{18}H_{26}NO_2S$, $[M+H^+]$: 320.1684; found: 320.1679.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 238 nm, retention times (min): 32.4 (major) and 33.5 (minor).

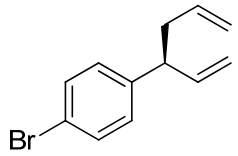


(+)-*N*-Allyl-4-methyl-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2j): The title compound was prepared from **1j** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column

chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.8) afforded **2j/3j** (91% yield, 70:30 ratio (b:l), 95:5 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.71 (m, 1H), 5.55 (m, 2H), 5.27-4.93 (m, 6H), 3.79 (m, 2H), 3.15 (dd, *J* = 7.2, 13.8 Hz, 1H), 2.99 (dd, *J* = 8.1, 13.9 Hz, 1H), 2.44 (m, 1H), 2.42 (s, 3H), 2.22 (m, 1H), 2.03 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.1, 139.3, 135.9, 133.0, 129.6 (2C), 127.2 (2C), 127.1, 119.0, 116.6, 116.4, 51.1, 51.0, 42.3, 36.5, 21.5.
$[\alpha]_D^{20}$ = +3.2 (*c* = 1.0, $CHCl_3$).
HRMS (ESI+, *m/z*): calcd. for $C_{17}H_{24}NO_2S$, $[M+H^+]$: 306.1528; found: 306.1522.
Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AS-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 240 nm, retention times (min): 19.2 (major) and 20.7 (minor).

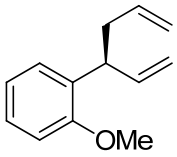


(-)-4-Methyl-*N*-(prop-2-ynyl)-*N*-(2-vinylpent-4-enyl)benzenesulfonamide (2k): The title compound was prepared from **1k** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.8) afforded **2k/3k** (86% yield, 37:63 ratio (b:l), 79:21 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.71 (dd, *J* = 4.4, 8.3 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 4H), 5.95-5.43 (m, 4H), 5.43-5.24 (m, 1H), 5.22-4.66 (m, 6H), 4.10 (dd, *J* = 2.4, 21.6 Hz, 4H), 3.76 (d, *J* = 6.8 Hz, 2H-linear), 3.19 (dd, *J* = 6.9, 13.5 Hz, 1H-branched), 3.09 (dd, *J* = 8.2, 13.5 Hz, 1H-branched), 2.55-2.43 (m, 1H), 2.41 (s, 6H), 2.31-2.18 (m, 1H), 2.17-2.03 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.4, 143.4, 139.0, 137.8, 136.2, 136.1, 135.8, 135.6, 129.4 (4C), 127.7 (4C), 123.7, 116.8, 116.6, 115.0, 76.7, 76.4, 73.8, 73.5, 49.9, 48.3, 41.9, 36.8, 36.6, 35.4, 33.1, 21.5 (2C).
HRMS (ESI+, *m/z*): calcd. for $C_{17}H_{22}NO_2S$, $[M+H^+]$: 304.1371; found: 304.1366.
Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 254 nm, retention times (min): 27.7 (minor) and 30.6 (major).



(+)-1-Bromo-4-(hexa-1,5-dien-3-yl)benzene (2l): The title compound was prepared from **1l** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, Et_2O/Pentane 2:98, R_f = 0.8) afforded **2l/3l** (81% yield, 46:54 ratio (b:l), 86:14 e.r.) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.41 (m, 8H), 7.22-7.05 (m, 8H), 6.28 (m, 2H), 5.96 (m, 2H), 5.69 (m, 1H), 5.03 (m, 6H), 3.36 (m, 1H-branched), 2.59 (m, 1H-branched), 2.46 (m, 1H-branched), 2.27 (m, 4H-linear). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 142.6, 140.9, 137.9, 136.7, 136.1, 131.5, 131.5, 131.5, 131.4, 130.9, 129.5, 129.4, 129.0, 127.5 (2C), 120.5, 116.5, 115.1, 115.0, 114.8, 39.6, 38.8, 33.4, 32.4.

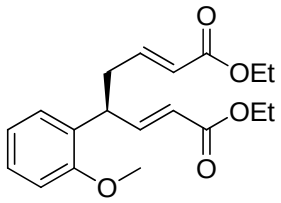
Enantiomeric excess determined by chiral GC analysis, CP-Chiralsil-Dex-CB column (25 m x 0.25 mm), initial temp. 50°C, then 10°C /min to 80°C, then 1°C /min to 140°C (hold for 5 min), then 10°C /min to 180°C (final temp), retention times (min): 102.3 (minor) and 104.3 (major).



(-)-1-(Hexa-1,5-dien-3-yl)-2-methoxybenzene (2m): The title compound was prepared from **1m** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column chromatography (SiO_2, Et_2O/Pentane 10:90, R_f = 0.7) afforded **2m/3m** (90% yield, 73:27 ratio (b:l), 95:5 e.r.) as a colorless oil. Enantiomeric ratio was determined for cross metathesis product **7m**. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.43 (dd, *J*= 1.0, 7.6 Hz, 1H), 7.18 (m, 3H), 6.90 (m, 3H), 6.75 (d, *J*= 15.5 Hz, 1H), 6.24 (m, 1H), 6.03 (m, 1H), 5.89 (m, 1H), 5.76 (m, 1H), 5.01 (m, 6H), 3.87 (m, 1H-branched), 3.85 (s, 3H), 3.83 (s, 3H), 2.49 (t, *J*= 7.2 Hz, 2H-branched), 2.35 (m, 2H-linear), 2.26 (m, 2H-linear). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 158.9, 156.3, 141.0, 138.3, 137.1, 132.1, 130.8, 127.9, 127.8, 127.1, 126.8, 126.4, 124.7, 120.6, 120.5, 115.6, 114.8, 114.2, 110.8, 110.7, 55.4 (2C), 42.1, 38.7, 33.7, 32.9.

$[\alpha]_D^{20}$ = -7.6 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{13}H_{17}O$, $[M+H^+]$: 189.1279; found: 189.1274.

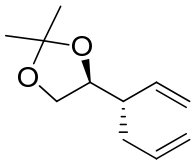


(+)-(*2E*,*6E*)-Diethyl 4-(2-methoxyphenyl)octa-2,6-dienedioate (7m): To a solution of **2m** (0.2 mmol) and ethyl acrylate (0.6 mmol) in dry dichloromethane (2 mL), HG-II catalyst (0.01 mmol, 5 mol%) was added and the mixture was heated at reflux for 24h. The mixture was cooled down to room temperature and the solvent was removed under reduced pressure to yield the crude product which was purified by flash chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.4) affording **7m** (65% yield, 95:5 e.r.) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.21 (dt, *J* = 1.6, 7.7 Hz, 1H), 7.09 (m, 2H), 6.88 (m, 3H), 5.81 (m, 2H), 4.16 (m, 4H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 2.68 (m, 1H), 2.37 (m, 1H), 1.26 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 166.4, 166.3, 156.7, 149.8, 146.1, 128.1, 128.0, 122.9, 122.3, 121.4, 120.8, 118.8, 60.3, 60.2, 55.4, 40.3, 36.2, 14.2 (2C).

$[\alpha]_D^{20}$ = +13.6 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{19}H_{25}O_5$, [M+H$^+$]: 333.1702; found: 333.1697.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 231 nm, retention times (min): 29.6 (major) and 34.5 (minor).

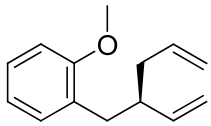


(+)-4-((S)-Hexa-1,5-dien-3-yl)-2,2-dimethyl-1,3-dioxolane (2n): The title compound was prepared from **1n** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, Et_2O/Pentane 1:30, R_f = 0.6) afforded ***anti*-2n** (81% yield, 07:84:15 ratio (**b*syn***:**b*anti***:**l**)) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 5.73 (m, 2H), 5.08 (m, 4H), 4.09 (c, *J* = 6.1 Hz, 1H), 3.99 (dd, *J* = 6.1, 7.9 Hz, 1H), 3.65 (t, *J* = 7.7 Hz, 1H), 2.23 (m, 2H), 2.13 (m, 1H), 1.40 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 137.6, 136.2, 117.0, 116.3, 108.8, 77.7, 67.3, 46.8, 35.6, 26.4, 25.4.

$[\alpha]_D^{20}$ = +12 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{11}H_{19}O_2$, [M+H$^+$]: 183.1385; found: 183.1380.

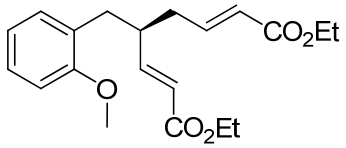
GC analysis was carried out to determine the b*syn*:b*anti*:l ratio.



(+)-1-Methoxy-2-(2-vinylpent-4-enyl)benzene (2o): The title compound was prepared from **1o** using (*S*,*R*,*R*)-**L4** as ligand. Purification by column chromatography (SiO_2, EtOAc/Pentane 2:98, R_f = 0.6) afforded **2o** (84% yield, 85:15 ratio (b:l), 91:09 e.r.) as a colorless oil. Enantiomeric ratio was determined for cross metathesis product **7o.** ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.18 (dt, *J* = 1.9, 7.9 Hz, 1H), 7.09 (dd, *J* = 1.6, 7.3 Hz, 1H), 6.86 (m, 2H), 5.81 (m, 1H), 5.68 (m, 1H), 5.02 (m, 2H), 4.89 (m, 2H), 3.81 (s, 3H), 2.74 (dd, *J* = 6.6, 13.3 Hz, 1H), 2.61 (dd, *J* = 7.7, 13.3 Hz, 1H), 2.48 (sex., *J* = 7.0 Hz, 1H), 2.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 157.7, 142.2, 137.2, 130.9, 128.9, 127.0, 120.1, 115.7, 114.1, 110.2, 55.2, 43.6, 38.8, 35.3.

$[\alpha]_D^{20}$ = +50 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{14}H_{19}O$, [M+H$^+$]: 203.1436; found: 203.1430.



(+)-*(2E,6E)*-Diethyl 4-(2-methoxybenzyl)octa-2,6-dienedioate (7o): To a solution of **2o** (0.2 mmol) and ethyl acrylate (0.6 mmol) in dry dichloromethane (2 mL), HG-II catalyst (0.01 mmol, 5 mol%) was added and the mixture was heated at reflux for 24h. The mixture was cooled down to room temperature and the solvent was removed under reduced pressure to yield the crude product which was purified by flash chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.7) affording **7o** (65% yield, 91:09 e.r.) as a colorless oil.

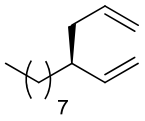
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.19 (dt, *J* = 1.6, 7.7 Hz, 1H), 7.03 (dd, *J* = 1.6, 7.3 Hz, 1H), 6.85 (m, 4H), 5.82 (d, *J* = 15.8 Hz, 1H), 5.68 (d, *J* = 15.8 Hz, 1H), 4.16 (m, 4H), 3.80 (s, 3H), 2.72 (m, 3H), 2.32 (m, 2H), 1.27 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$), δ:

166.4, 166.3, 157.5, 151.0, 146.2, 130.8, 127.8, 127.2, 123.1, 121.4, 120.3, 110.3, 60.2 (2C), 55.1, 41.6, 36.2, 35.0, 14.2, 14.2.

$[\alpha]_D^{20}$ = -16 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{20}H_{27}O_5$, $[M+H^+]$: 347.1858; found: 347.1853.

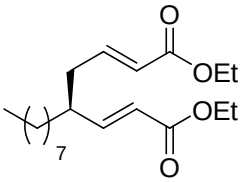
Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 98:2, 40 °C, 234 nm, retention times (min): 28.6 (minor) and 32.3 (major).



(+)-4-Vinyldodec-1-ene (2p): The title compound was prepared from **1p** using (*R*,*S*,*S*)-**L4** as ligand. Purification by column chromatography (SiO_2, Et_2O/Pentane 1:99, R_f = 0.9) afforded **2p/3p** (84% yield, 88:12 ratio (b:l), 97:3 e.r.) as a colorless oil. Enantiomeric ratio was determined for cross metathesis product **7p**. ^1H NMR (400 MHz, $CDCl_3$), δ: 5.76 (m, 1H), 5.59 (m, 1H), 4.98 (m, 4H), 2.17-1.94 (m, 3H), 1.26 (m, 14H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 143.6, 138.0, 116.3, 114.8, 44.5, 40.3, 35.0, 32.7, 30.5, 30.4, 30.1, 27.9, 23.5, 14.9.

$[\alpha]_D^{20}$ = +2.0 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{14}H_{27}$, $[M+H^+]$: 195.2113; found: 195.2107.

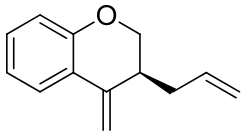


(-)-*(2E,6E)*-Diethyl 4-octylocta-2,6-dienedioate (7p): To a solution of **2p** (0.2 mmol) and ethyl acrylate (0.6 mmol) in dry dichloromethane (2 mL), HG-II catalyst (0.01 mmol, 5 mol%) was added and the mixture was heated at reflux for 24h. The mixture was cooled down to room temperature and the solvent was removed under reduced pressure to yield the crude product which was purified by flash chromatography (SiO_2, EtOAc/Pentane 10:90, R_f = 0.5) affording **7p** (71% yield, 97:3 e.r.) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$), δ: 6.84 (dt, *J* = 7.1, 15.5 Hz, 1H), 6.74 (dd, *J* = 8.3, 15.6 Hz,

1H), 5.79 (m, 2H), 4.18 (m, 4H), 2.30 (m, 3H), 1.26 (m, 17H), 0.87 (t, J = 6.8 Hz, 3H) . ^{13}C NMR (101 MHz, $CDCl_3$), δ: 166.4, 166.3, 151.4, 146.0, 123.1, 121.7, 60.3, 60.2, 41.6, 36.9, 33.9, 31.8, 29.5, 29.4, 29.2, 27.0, 22.6, 14.2 (2C), 14.0.

HRMS (ESI+, *m/z*): calcd. for $C_{20}H_{35}O_4$, [M+H$^+$]: 339.2535; found: 339.2530.

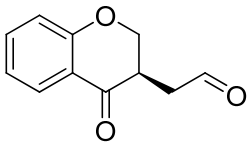
Enantiomeric excess was determined by chiral HPLC analysis, Chiralpak AD-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 227 nm, retention times (min): 16.7 (minor) and 17.6 (major).



(-)-3-Allyl-4-methylenechromene (4): TBAB (2 g), TBAA (0.9 g, 3 mmol), $Pd(OAc)_2$ (3 mol%) and (+)-**2a** (366 mg, 1.37 mmol) were stirred and heated at 100 °C for 1h. Water (3 mL) and EtOAc (3 mL) were added and, after cooling to r.t., the organic phase separated. The aqueous phase was extracted with EtOAc (2 x 5 mL). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure to yield the crude product which was purified by flash chromatography (SiO_2, EtOAc/Pentane 1:99, R_f = 0.5). 78% yield, ratio exo:endo = 99:1. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.47 (dd, J = 1.6, 7.7 Hz, 1H), 7.09 (dt, J = 1.6, 7.7 Hz, 1H), 6.81 (dt, J = 1.3, 7.5 Hz, 1H), 6.76 (dd, J = 1.0, 8.2 Hz, 1H), 5.76 (m, 1H), 5.44 (s, 1H), 5.02 (m, 1H), 4.98 (m, 1H), 4.82 (s, 1H), 4.08 (d, J = 3.5 Hz, 2H), 2.49 (m, 1H), 2.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 153.9, 140.6, 135.9, 129.4, 124.9, 120.9, 120.8, 117.1, 116.9, 106.9, 69.2, 40.2, 34.9.

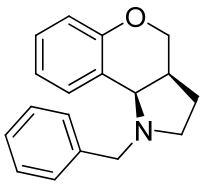
$[\alpha]_D^{20}$ = -44 (c = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{13}H_{15}O$, [M+H$^+$]: 187.1123; found: 187.1117.



2-(4-Oxochroman-3-yl)acetaldehyde (5): Dried ozone gas was passed through a colorless solution of **4** (112 mg) in CH_2Cl_2 (5 mL) at -78 °C for 20 min until the resulting

solution became blue-white. After addition of CH_2Cl_2 (8 mL), nitrogen gas was passed through at -78 °C until the resulting solution became colorless. Dimethyl sulfide (1 mL) was added at -78 °C, and the resulting solution was stirred at 0 °C for 10 min, and at room temperature for 18 h. The whole was mixed with CH_2Cl_2 (8 mL) and water (15 mL), and the aqueous layer was extracted with CH_2Cl_2 (20 mL) twice. The organic extracts were combined, washed with brine (20 mL), dried over Na_2SO_4, and evaporated to dryness. The residue was subjected to column chromatography (SiO_2, EtOAc/Pentane 5:95) affording **5** (81% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 9.86 (s, 1H), 7.86 (dd, *J* = 1.6, 7.9 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.54 (dd, *J* = 5.4, 11.1 Hz, 1H), 4.22 (t, *J* = 11.5 Hz, 1H), 3.43 (m, 1H), 3.06 (dd, *J* = 5.1, 18.3 Hz, 1H), 2.53 (dd, *J* = 7.2, 18.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 198.8, 192.7, 161.7, 136.1, 127.3, 121.5, 120.4, 117.8, 70.1, 40.7, 39.4. HRMS (ESI+, *m/z*): calcd. for $C_{11}H_{11}O_3$, [M+H$^+$]: 191.0708; found: 191.0703.



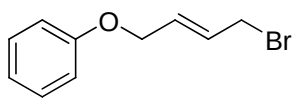
(+)-1-Benzyl-1,2,3,3a,4,9b-hexahydrochromeno[4,3-b]pyrrole (6): To a solution of aldehyde **5** (23 mg, 0.12 mmol) in MeOH (3 mL) were added sequentially benzylamine hydrochloride (95.1mg, 0.66 mmol) and then $NaBH_3CN$ (7 mg, 0.11 mmol). After stirring for 30 min, an additional portion of $NaBH_3CN$ (7 mg, 0.11 mmol) was added and stirring was continued for 1 h. A third portion of $NaBH_3CN$ (21 mg, 0.33 mmol) was then added, and stirring was continued overnight. After removing the MeOH, CH_2Cl_2 was added and the resulting organic solution was washed with sat. aq. $NaHCO_3$ solution, dried and concentrated. The resulting mixture was purified by column chromatography (SiO_2, EtOAc/Pentane 10:90) afforded **6** (95% yield, 96:4 e.r.) as a waxy solid. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.24 (m, 7H), 6.92 (m, 2H), 4.41 (d, *J* = 12.7 Hz, 1H), 4.07 (m, 2H), 3.23 (m, 2H), 2.88 (dt, *J* = 2.8, 9.1 Hz, 1H), 2.45 (m, 1H), 2.18 (c, *J* = 8.9 Hz, 1H), 2.03 (m, 1H), 1.40 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$), δ: 155.4, 139.9, 132.0, 128.8, 128.5 (2C), 128.0 (2C), 126.7, 121.5, 119.7, 116.8, 67.6, 61.4, 57.3, 51.2, 34.4, 24.4.

$[\alpha]_D^{20}$ = +96 (*c* = 1.0, $CHCl_3$).

HRMS (ESI+, *m/z*): calcd. for $C_{18}H_{20}NO$, $[M+H^+]$: 266.1545; found: 266.1539.

Enantiomeric excess was determined by chiral HPLC analysis, Chiralcel OJ-H column, *n*-heptane/*i*-PrOH 99:1, 40 °C, 225 nm, retention times (min): 17.4 (major) and 20.7 (minor).

6. NMR spectra of new compounds



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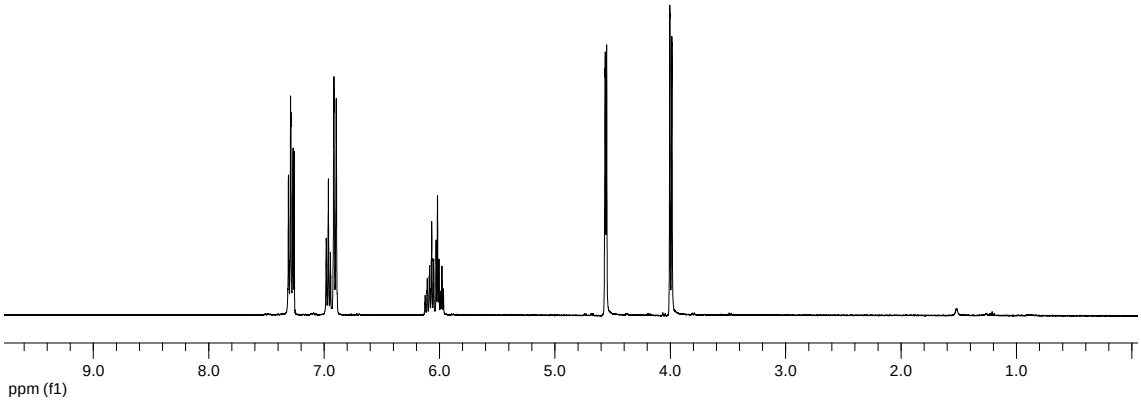
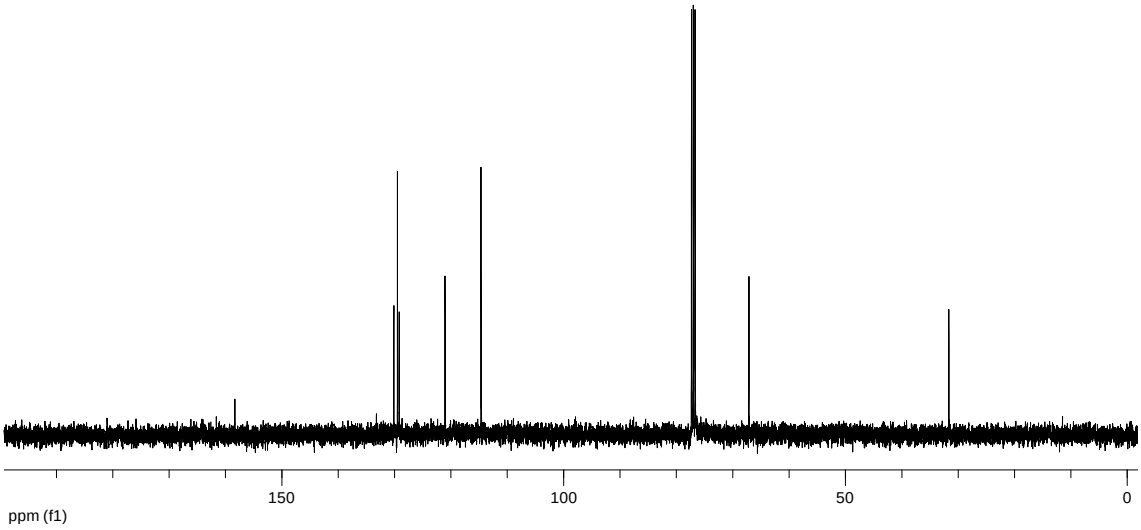
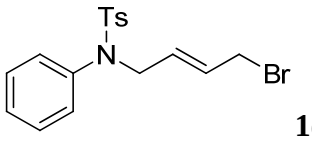
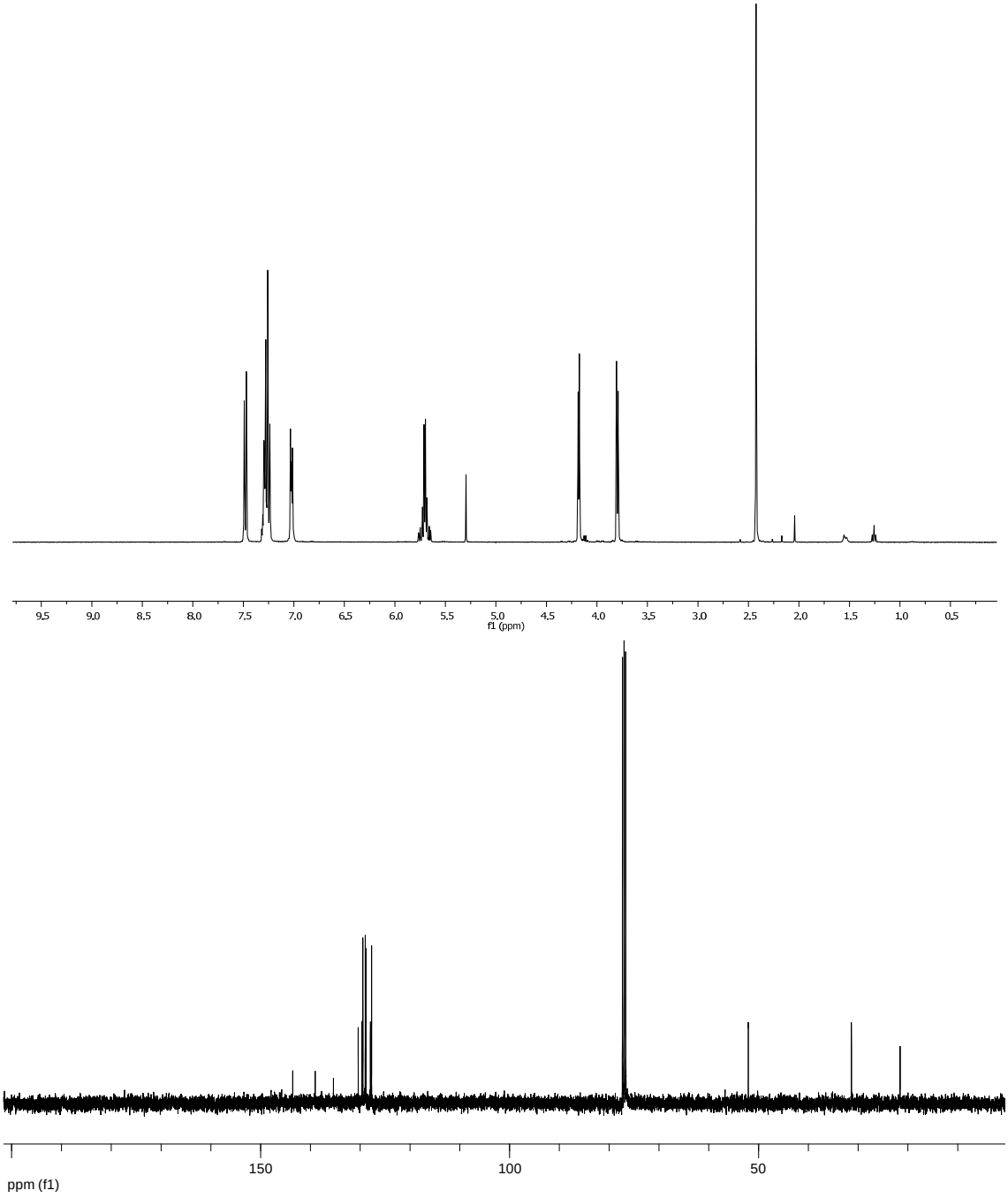





Ts
N
Br

1d


9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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5.0
4.5
4.0
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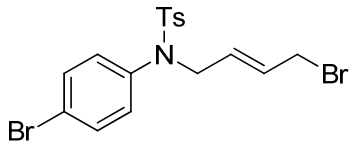
1.5
1.0
0.5
f1 (ppm)
150
100
50
ppm (f1)



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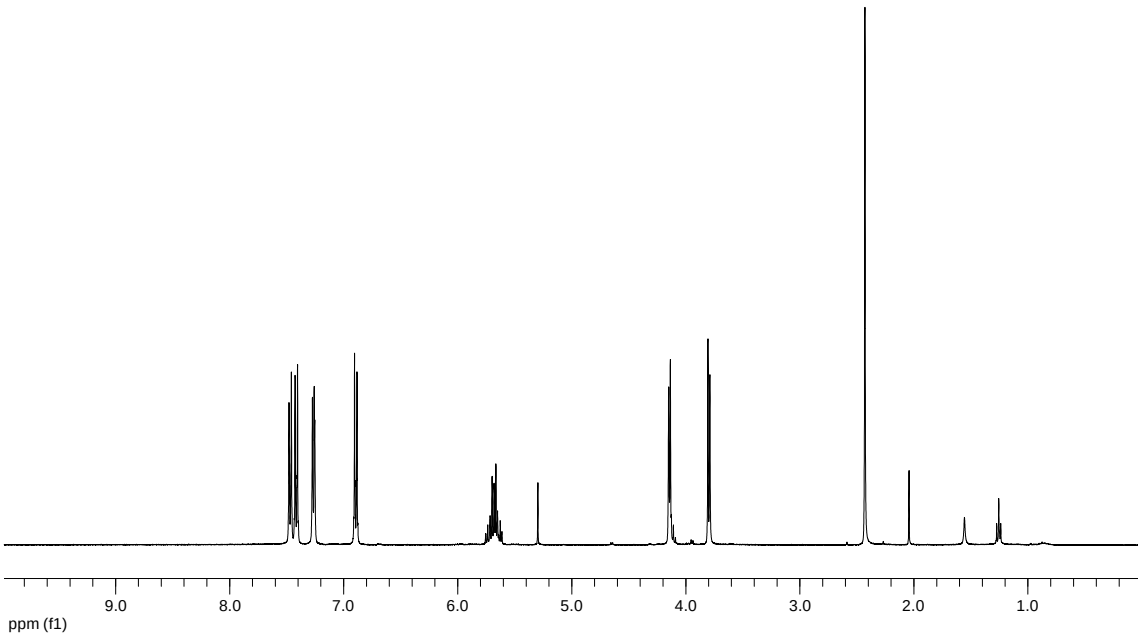

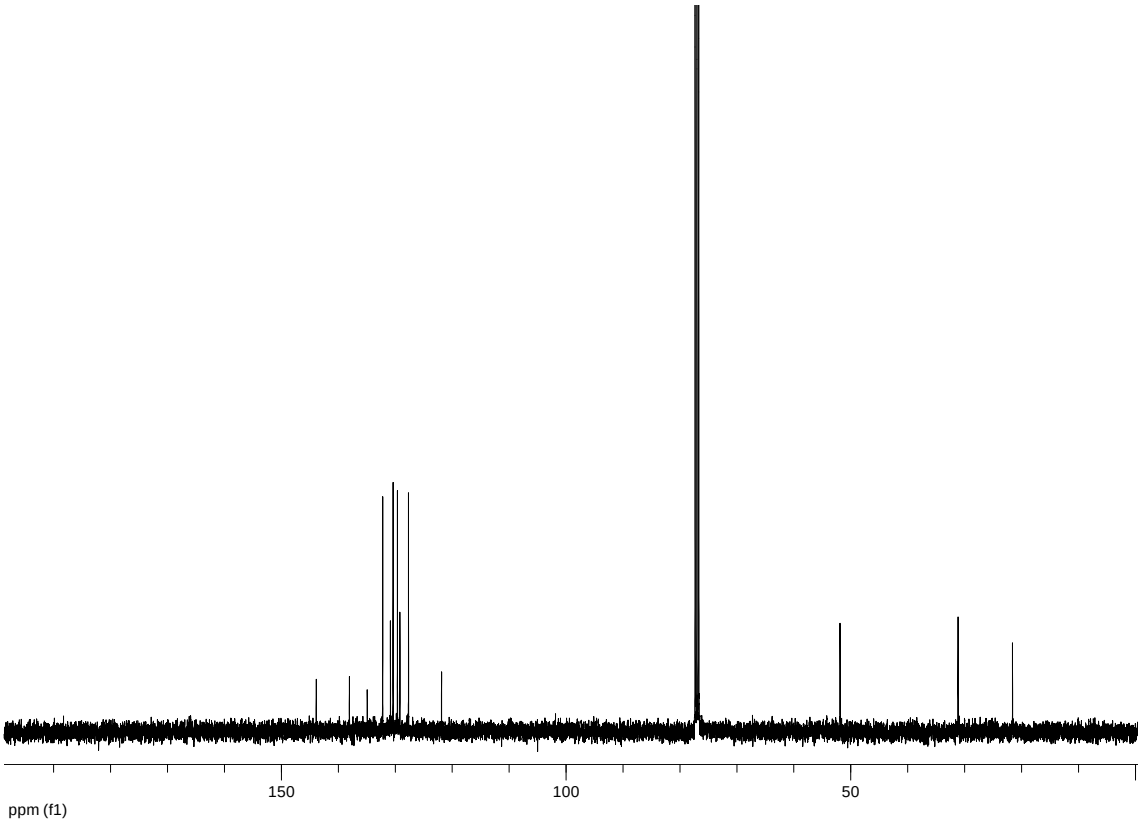

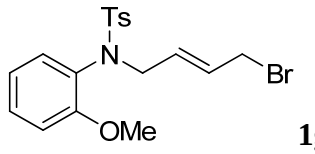

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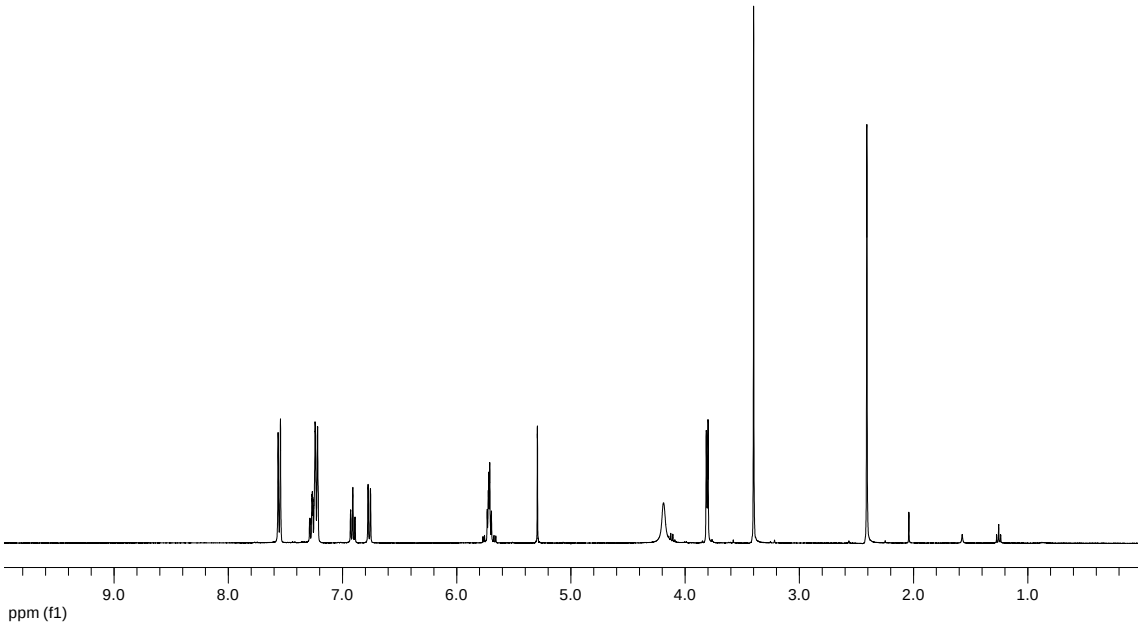

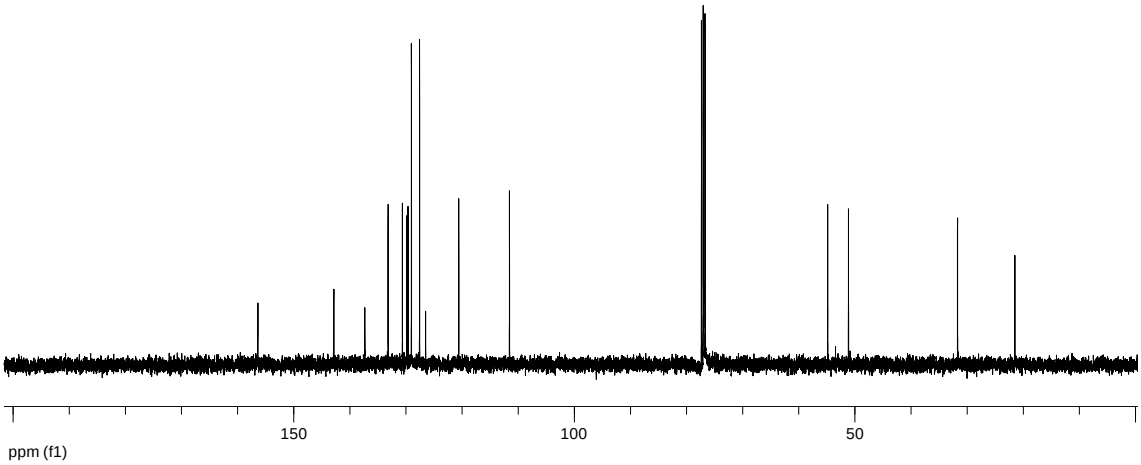

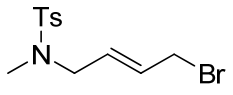

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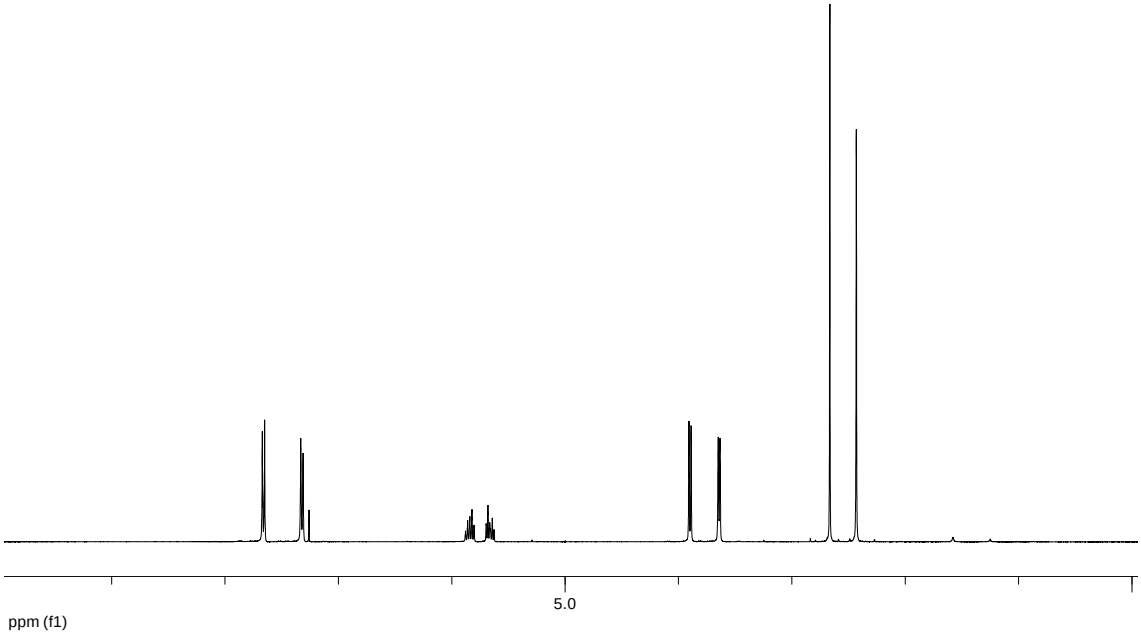

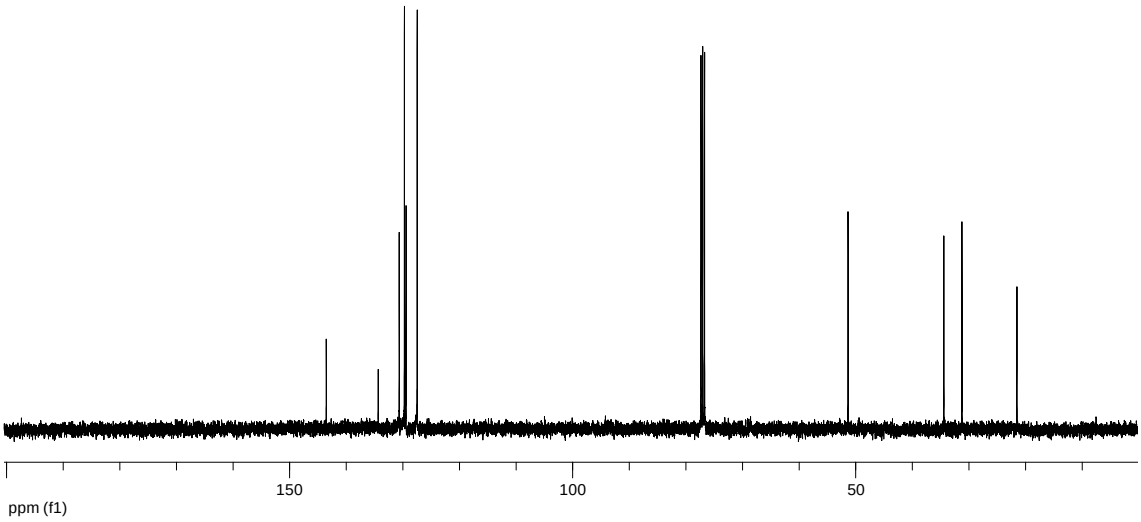

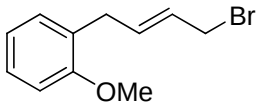

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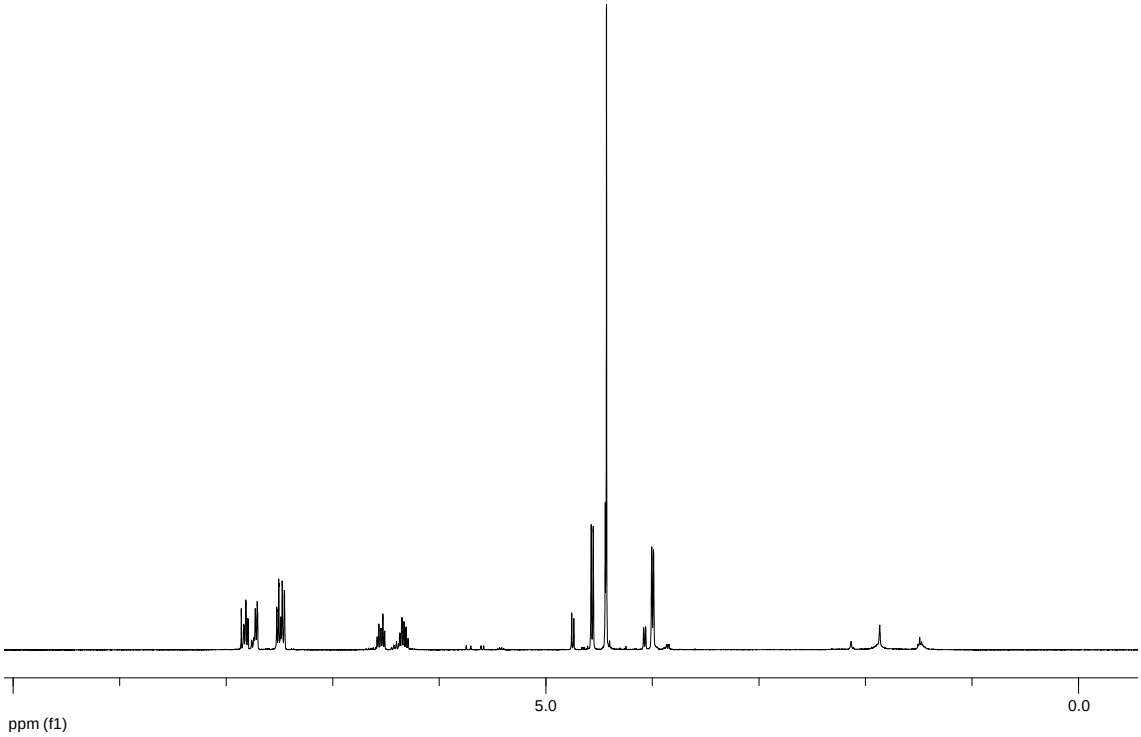

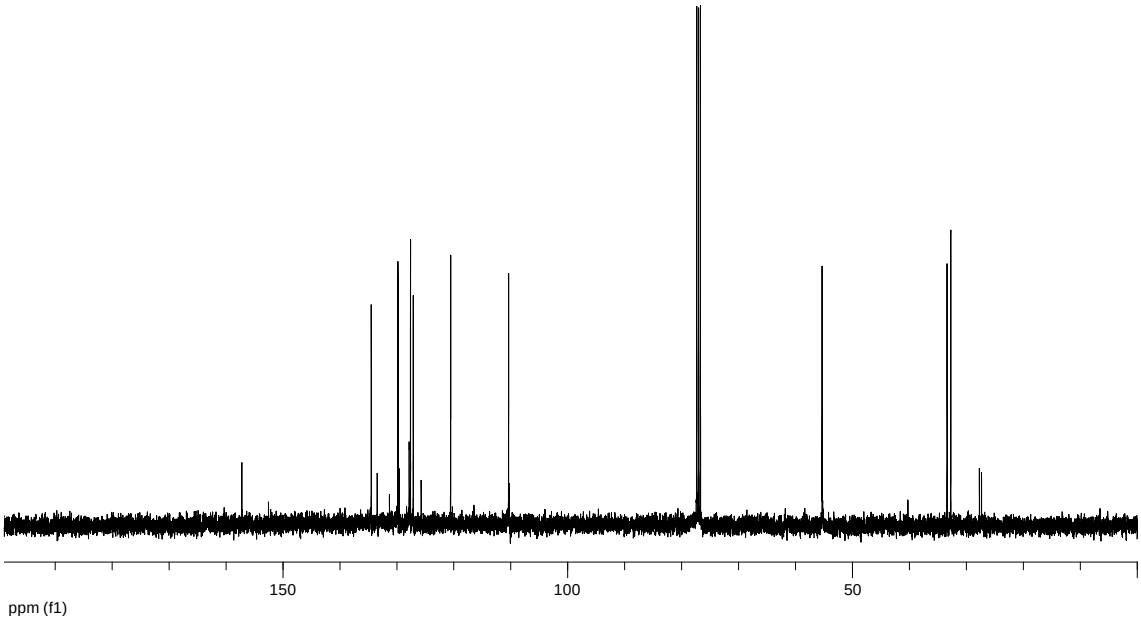

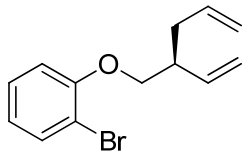

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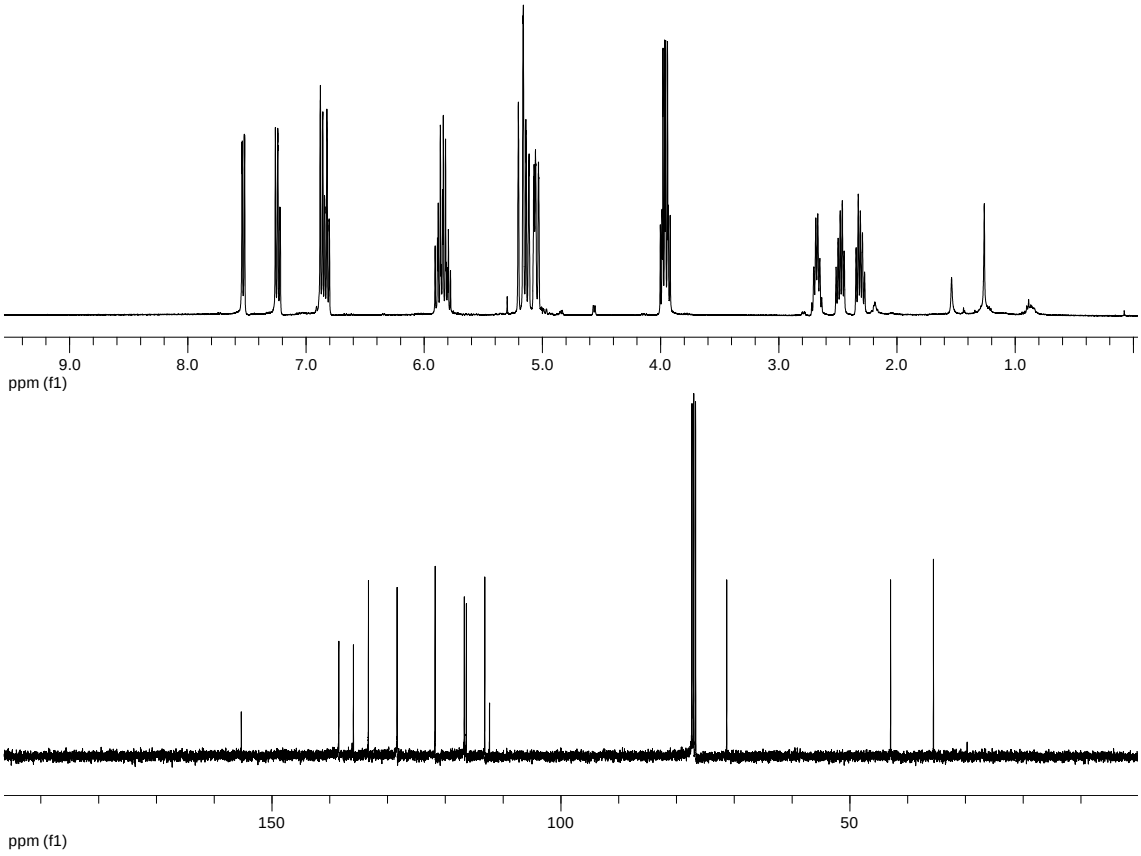

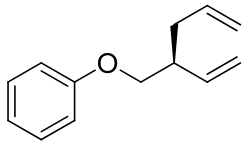

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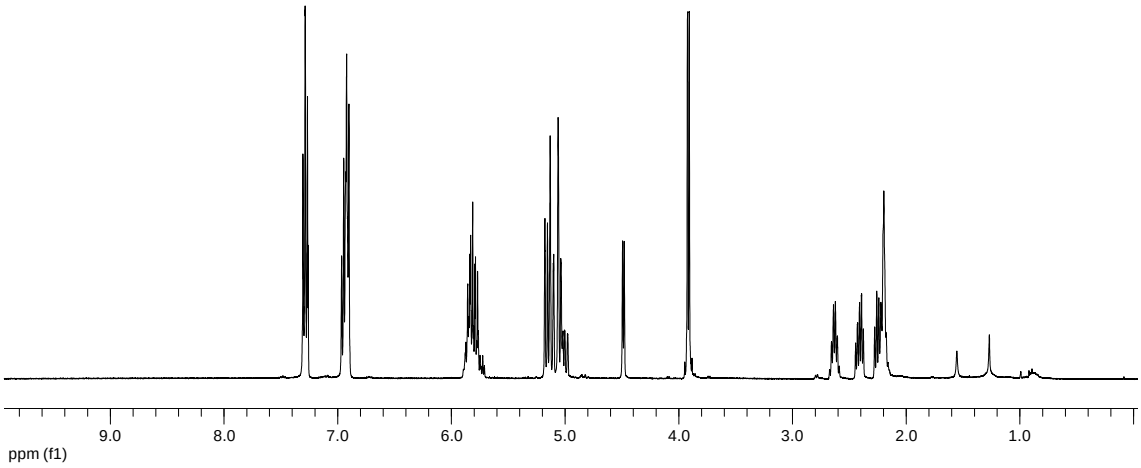

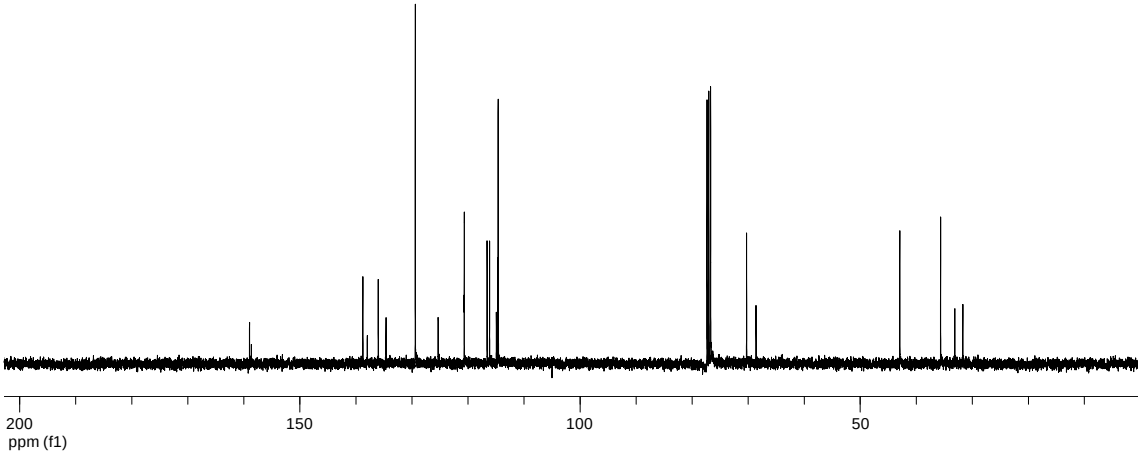

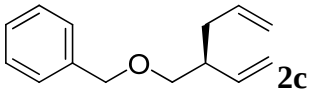

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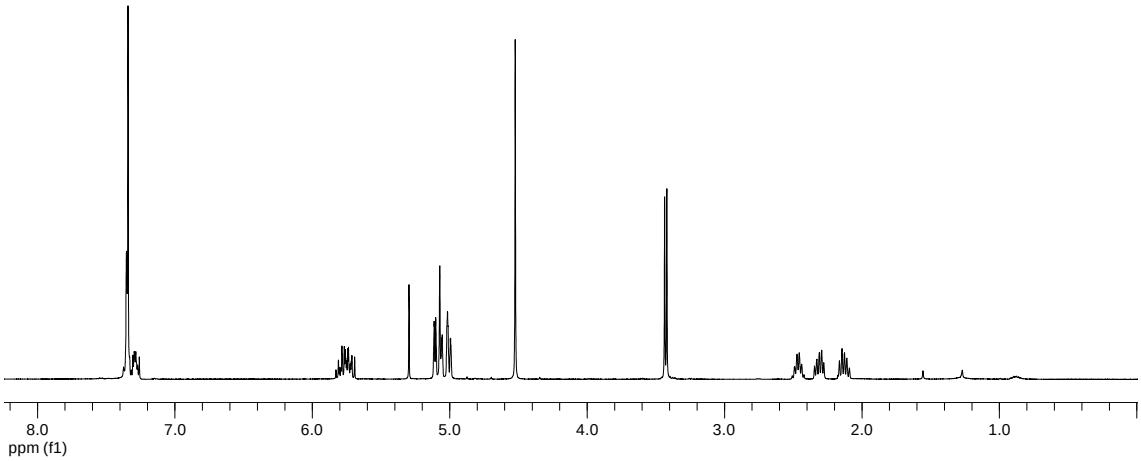

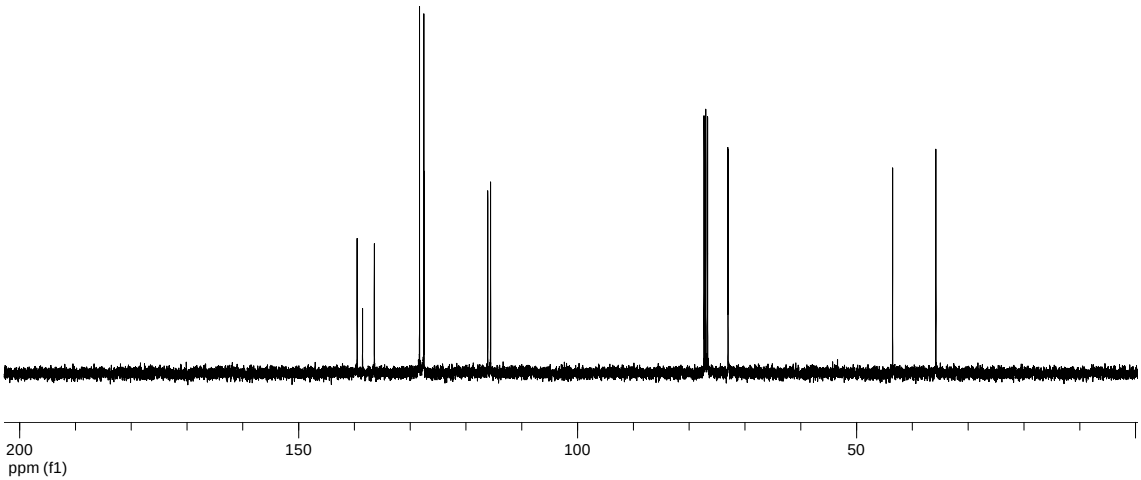

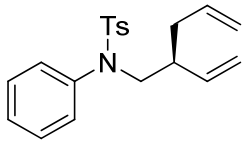

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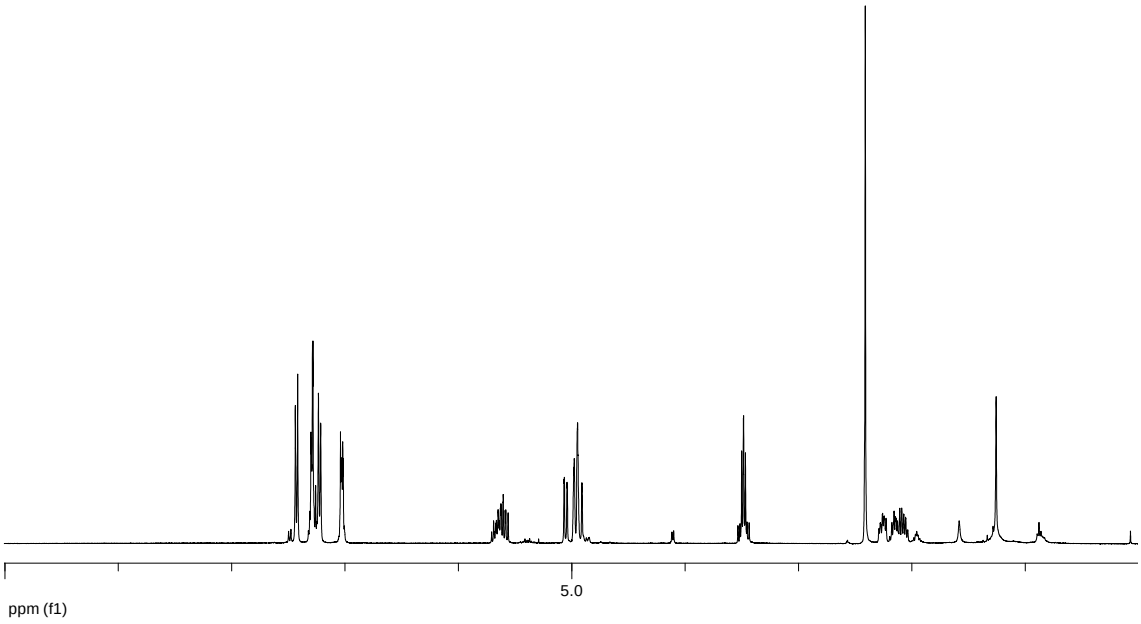

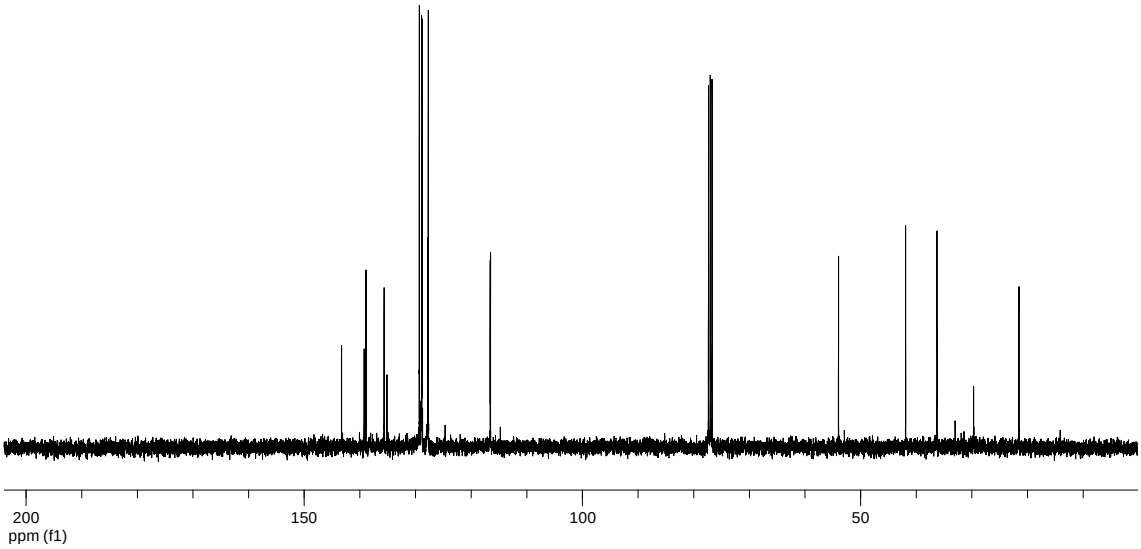

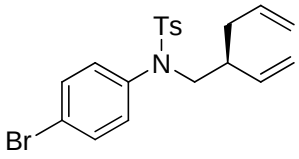

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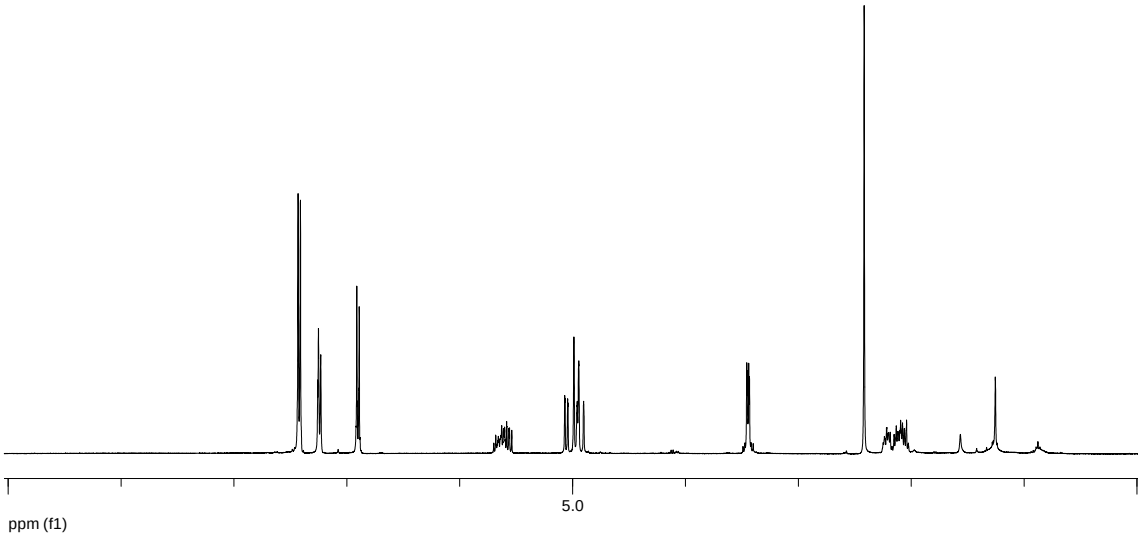

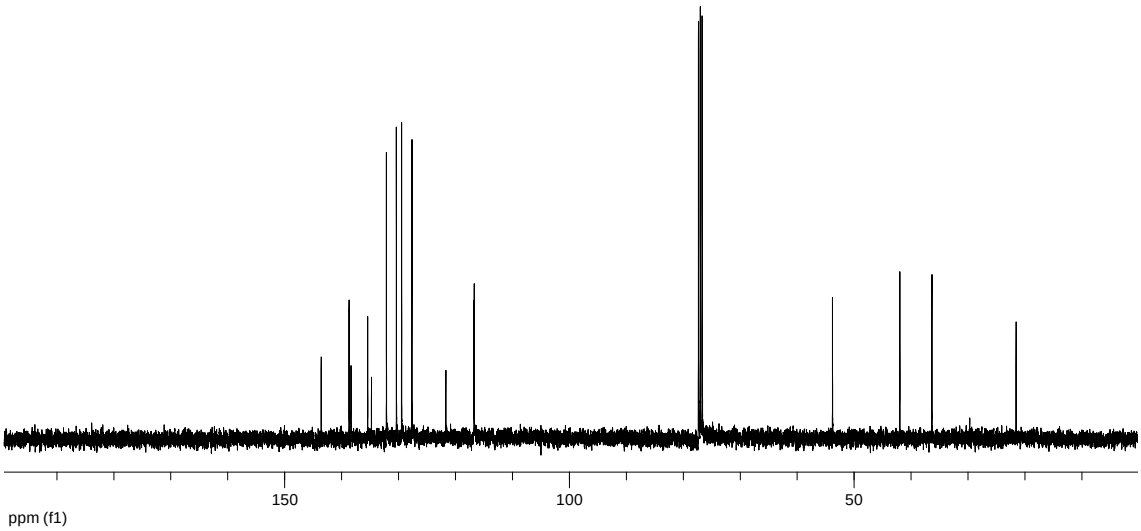

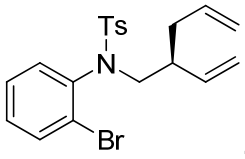

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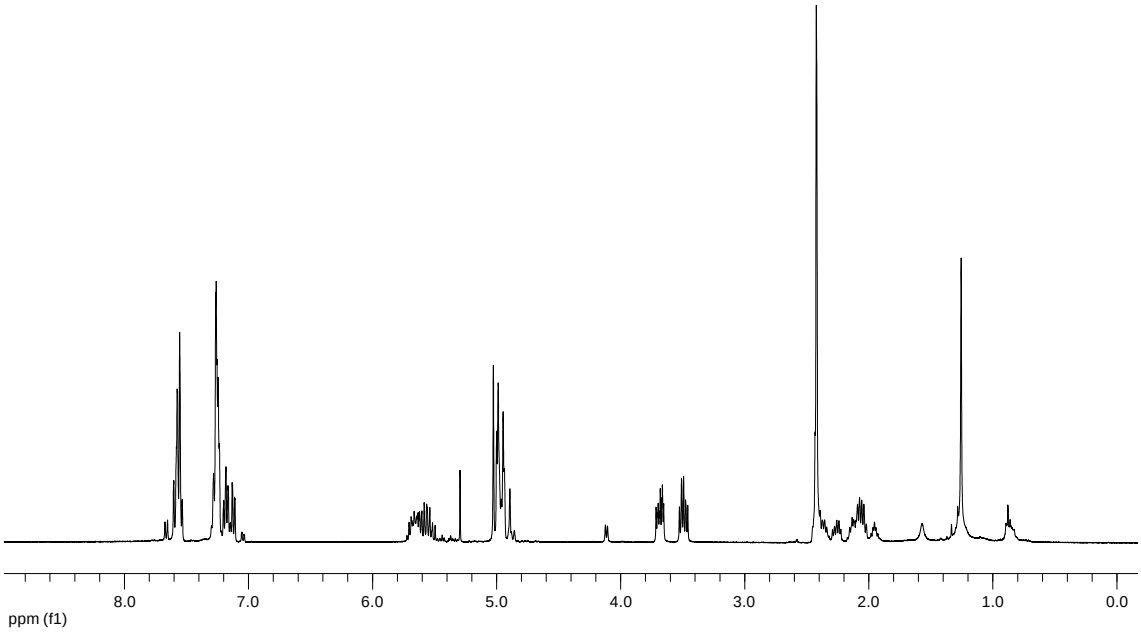

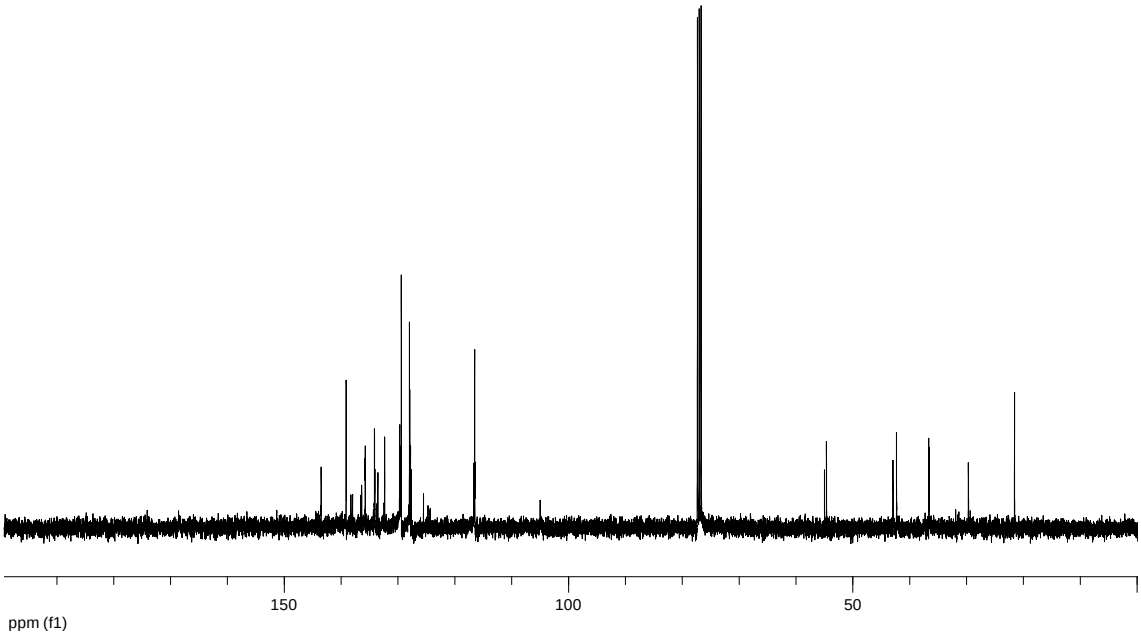

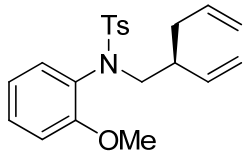

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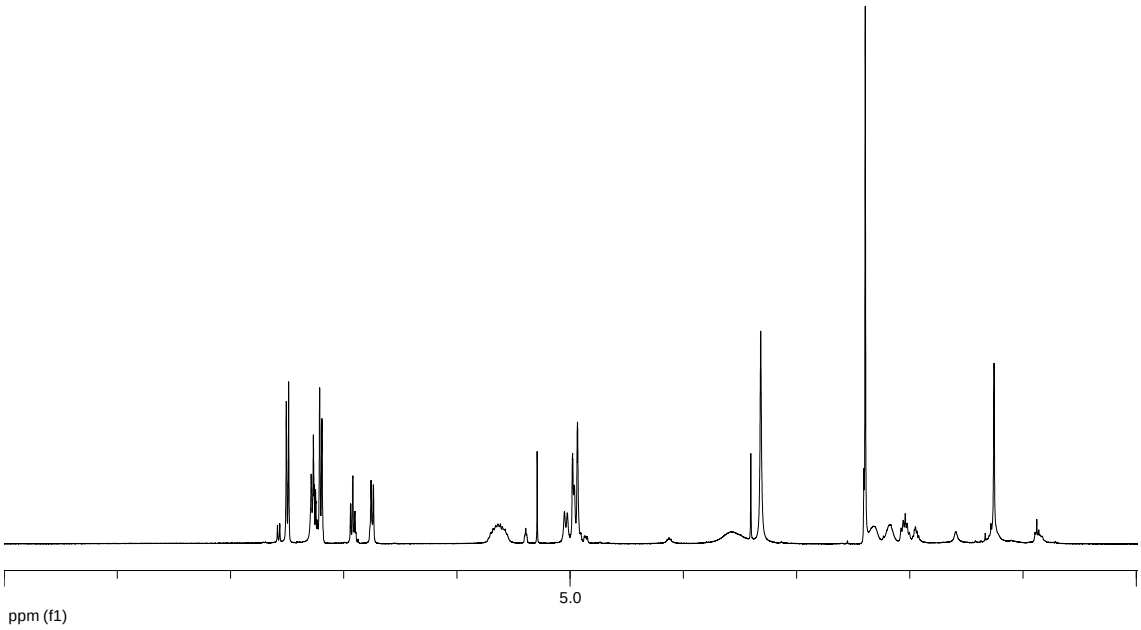

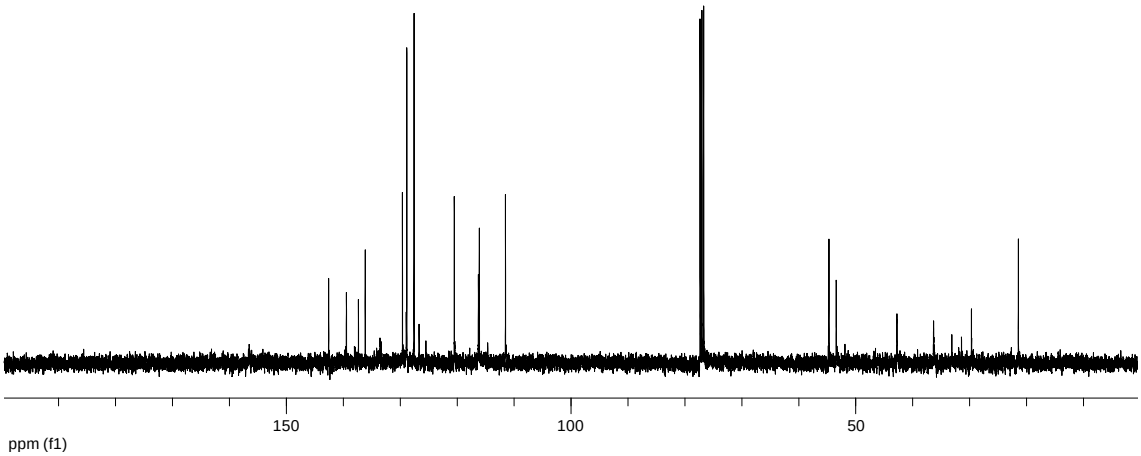

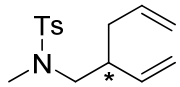

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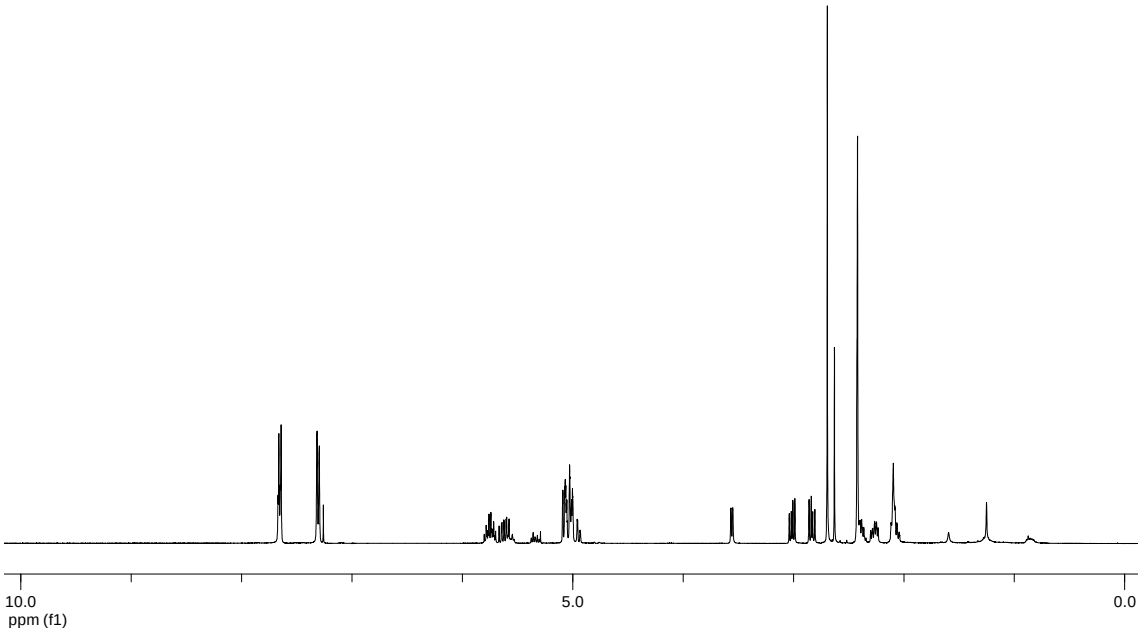

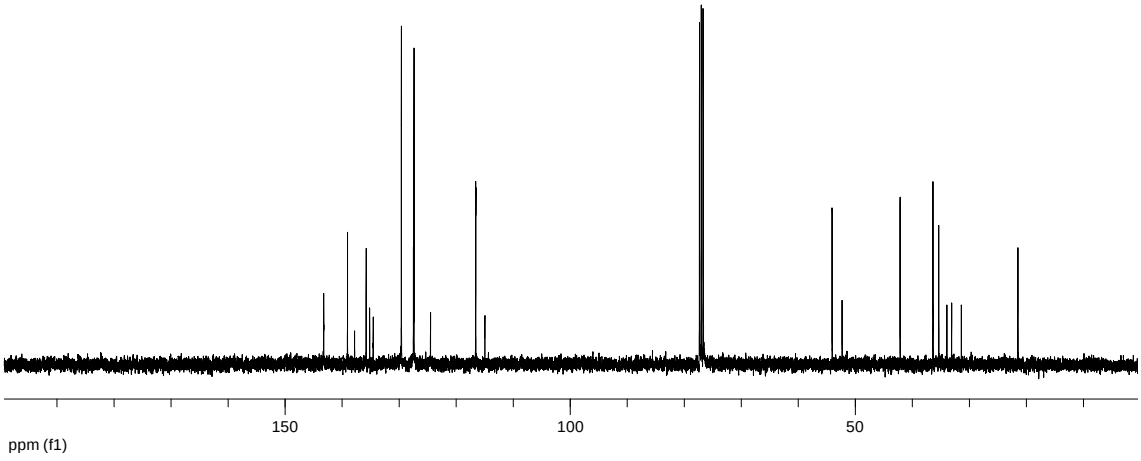

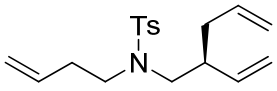

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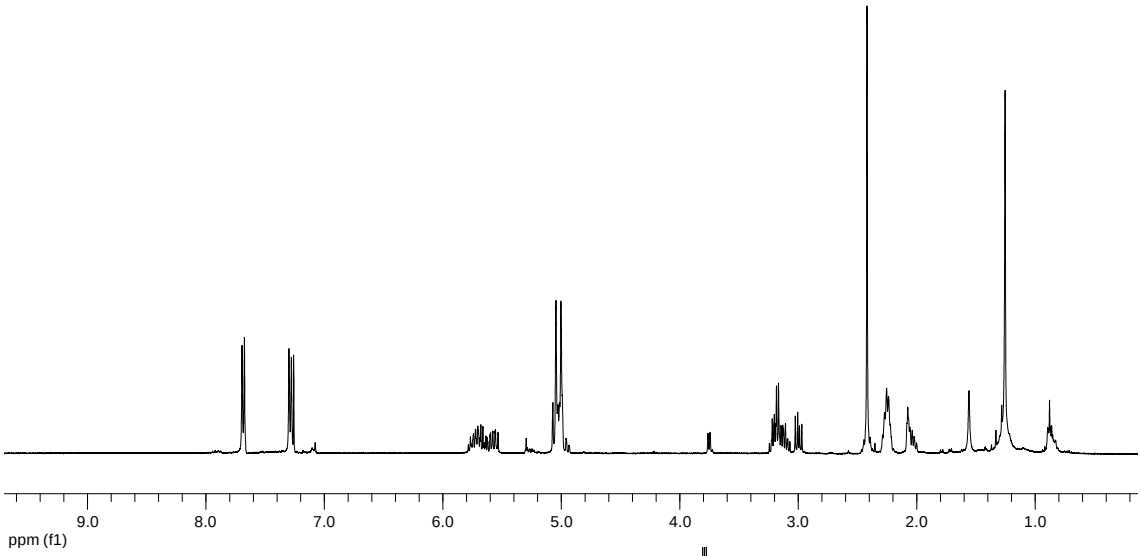

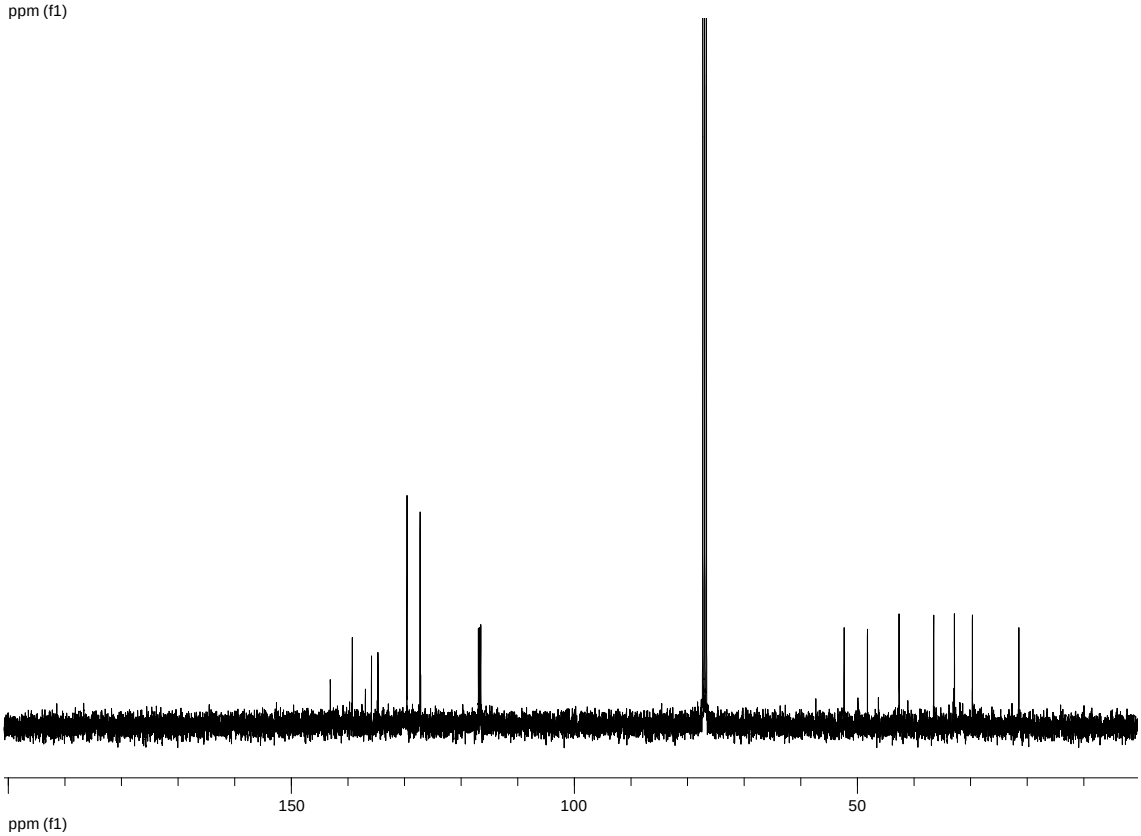

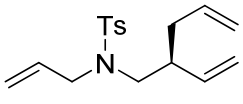

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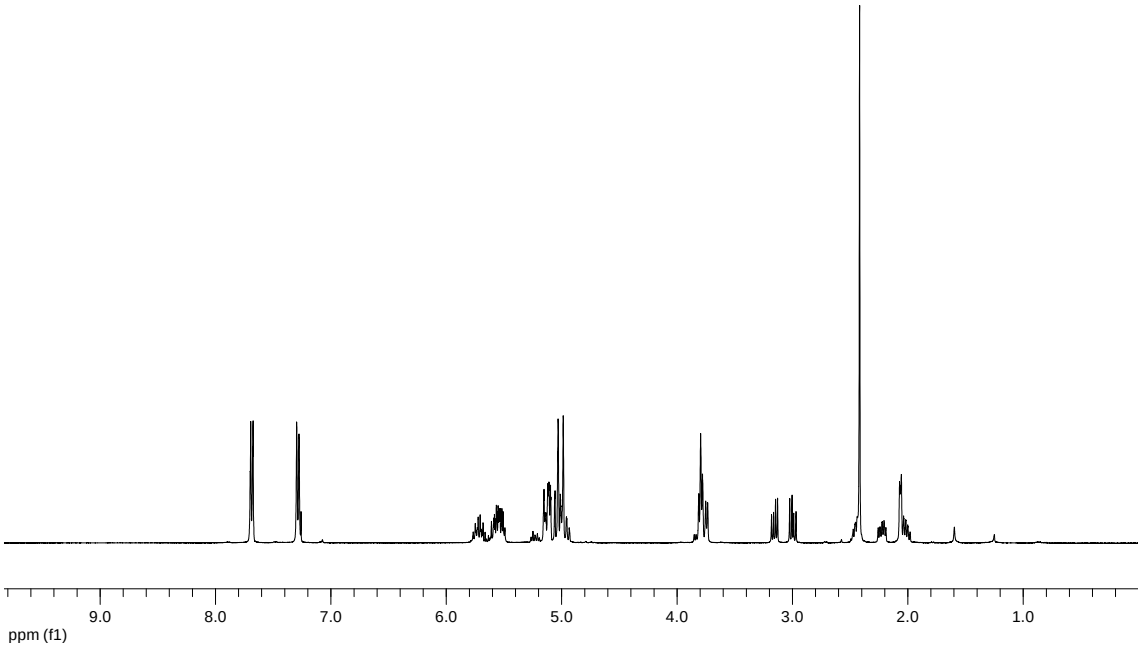

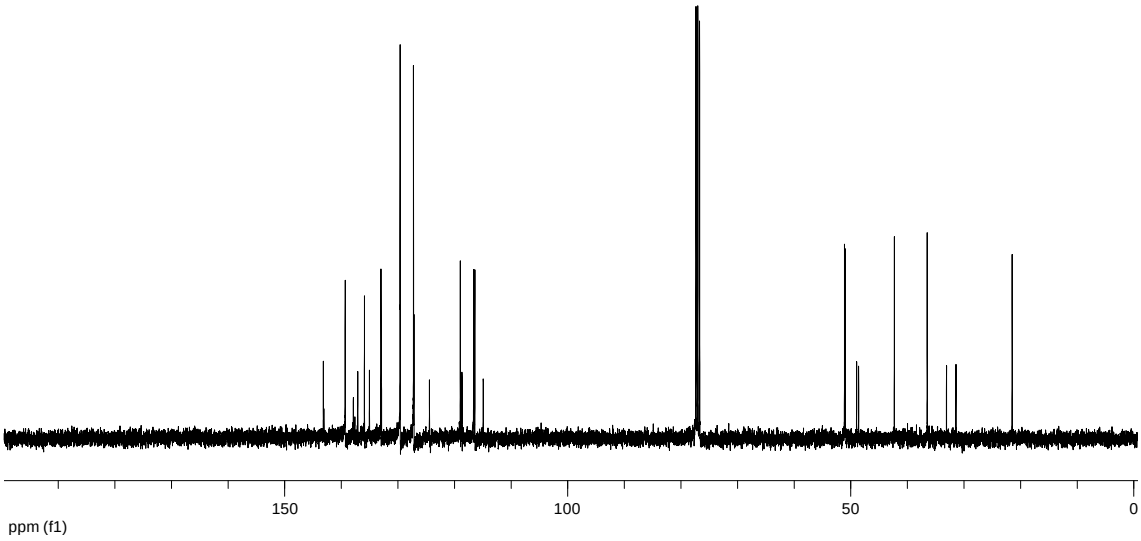

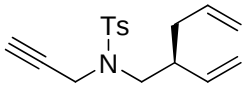
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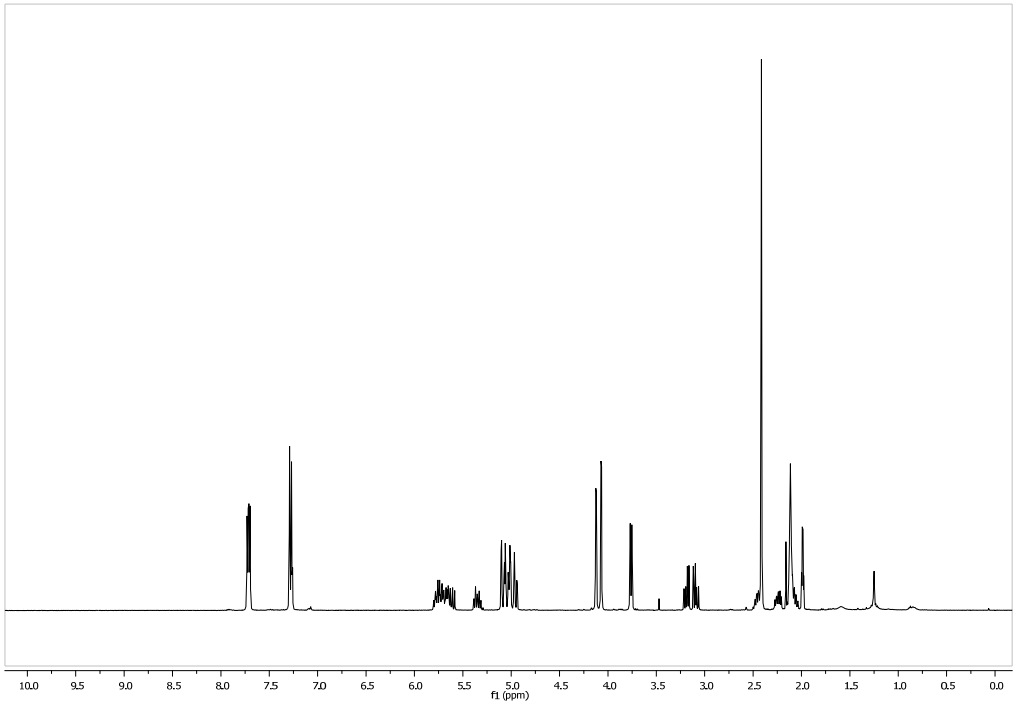
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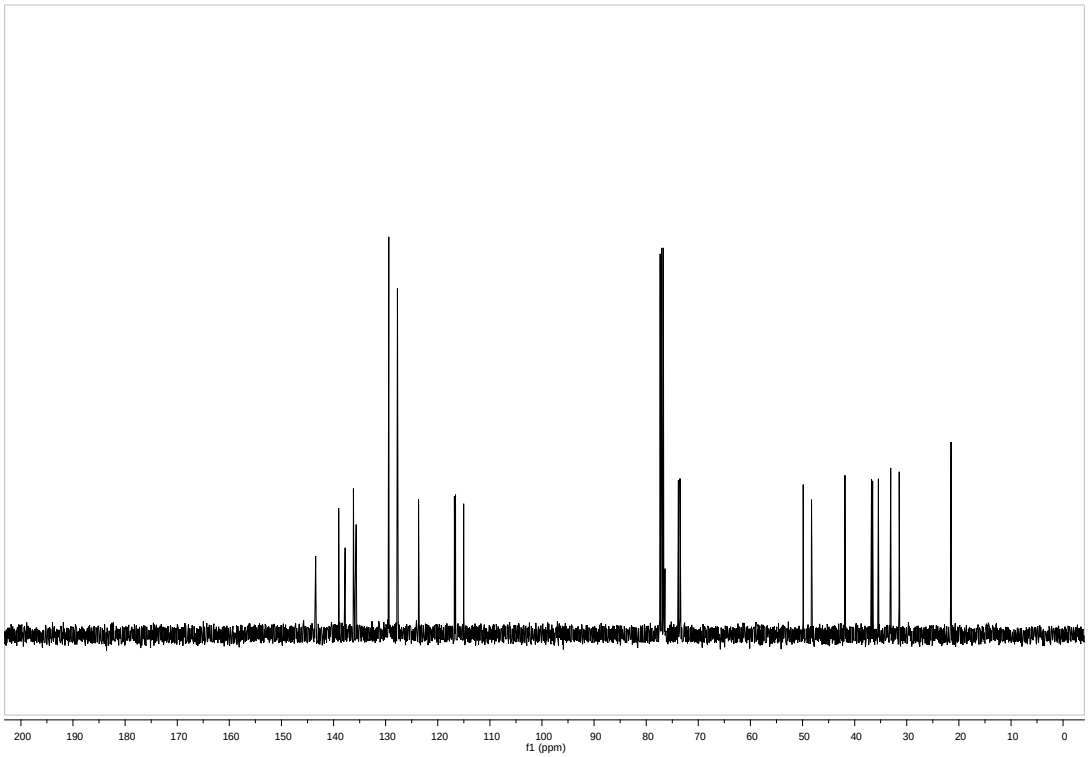
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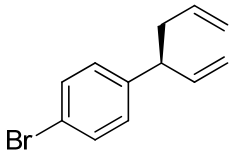

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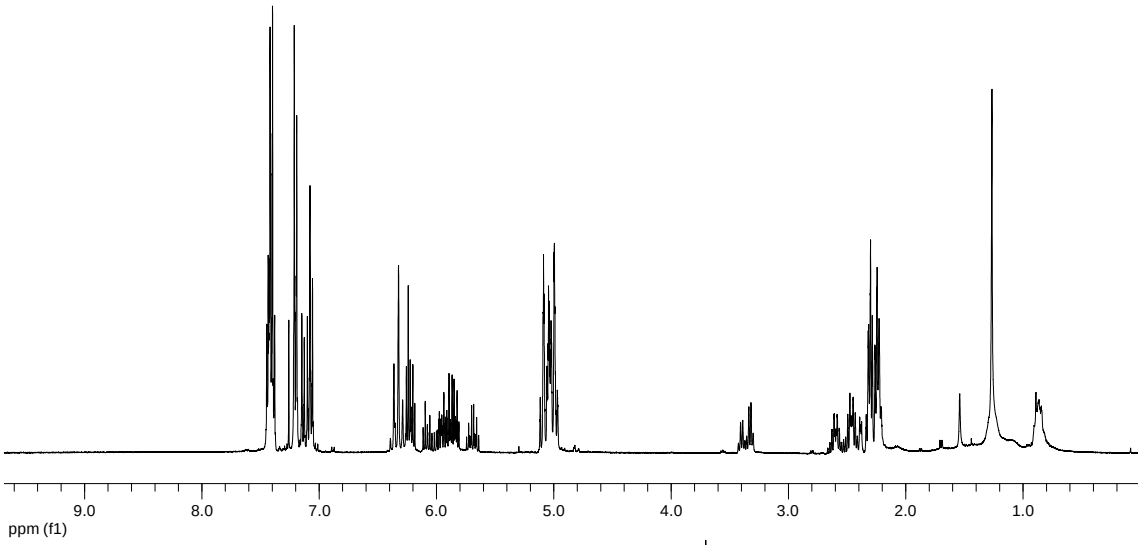

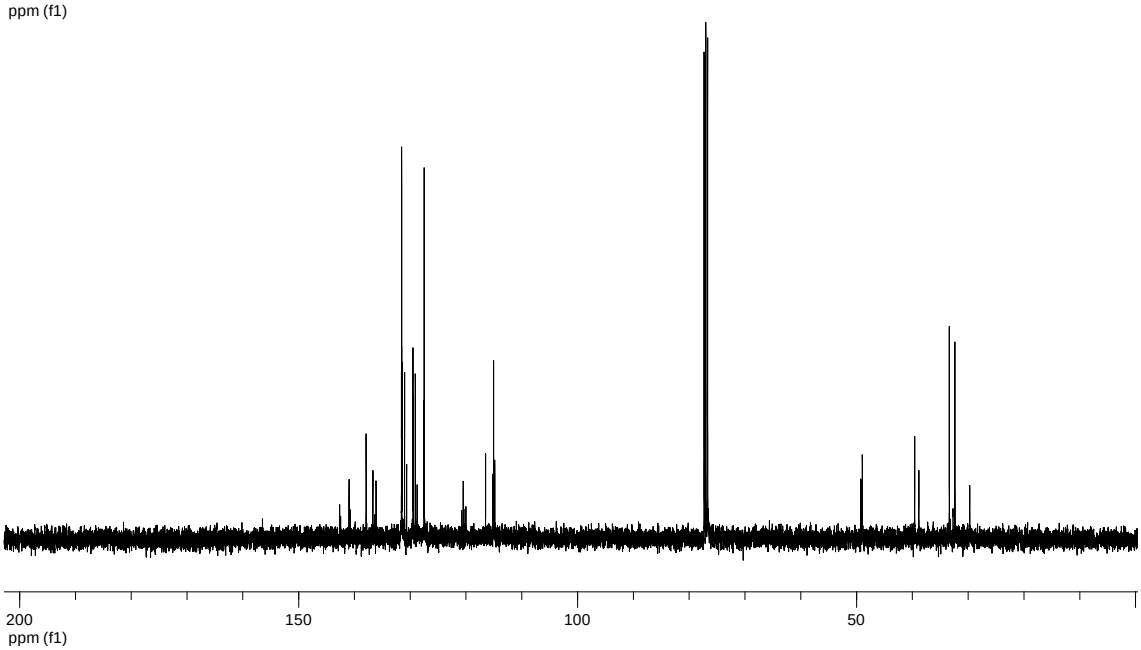

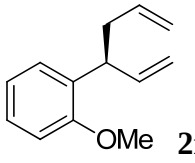

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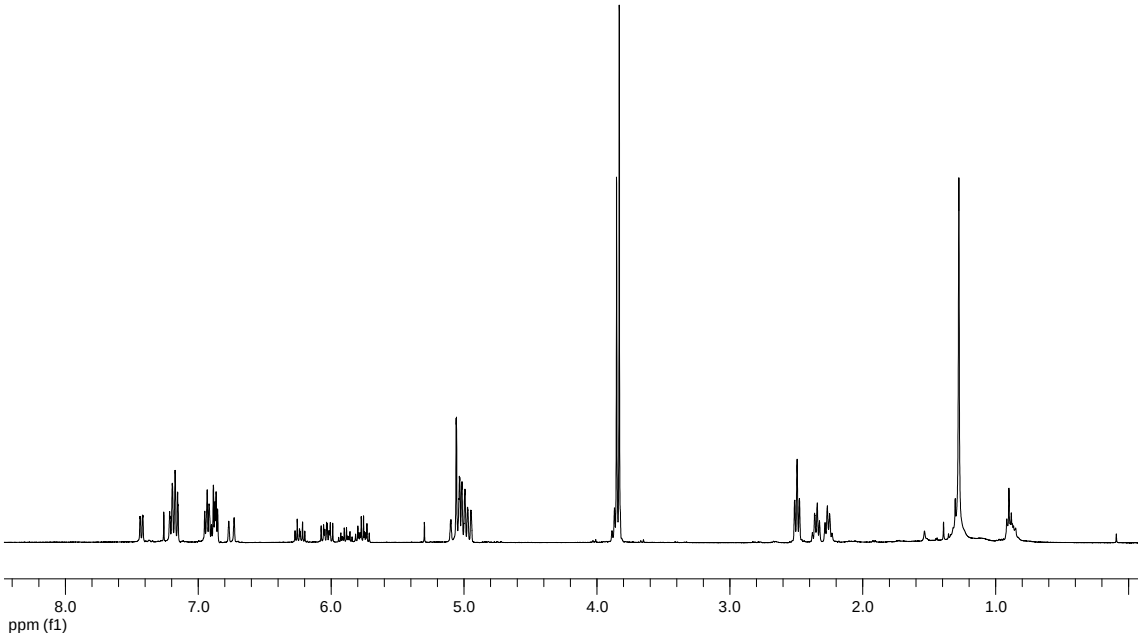

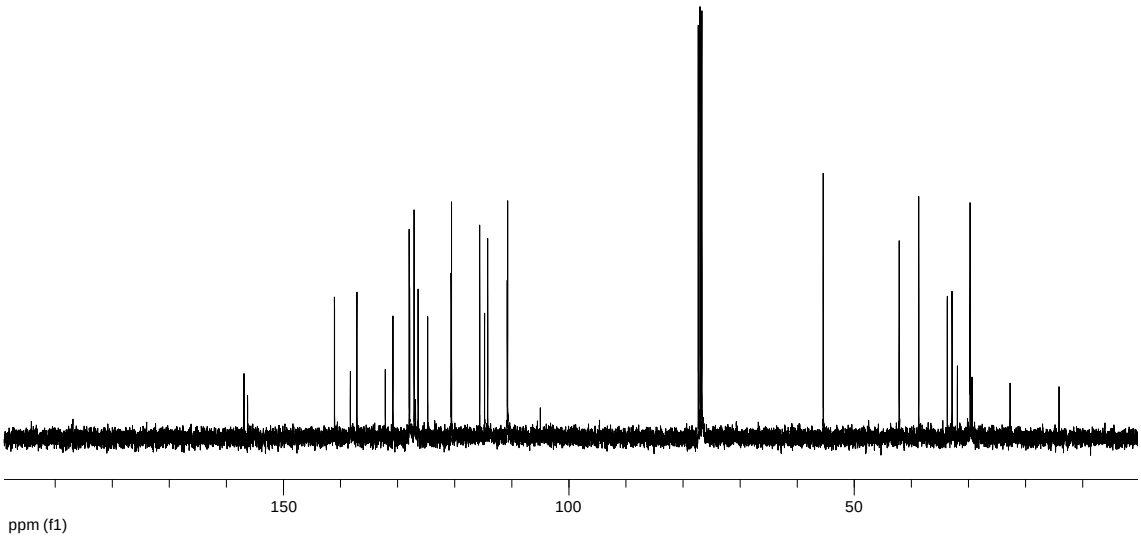

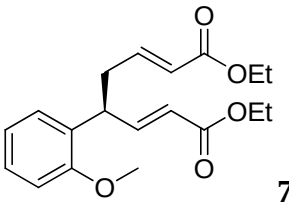
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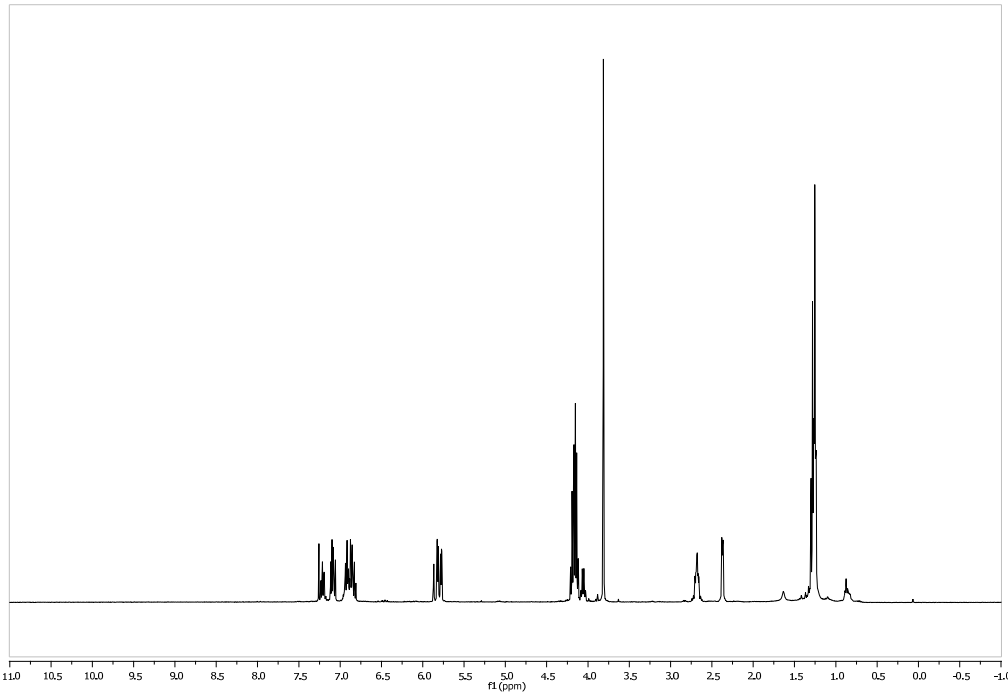
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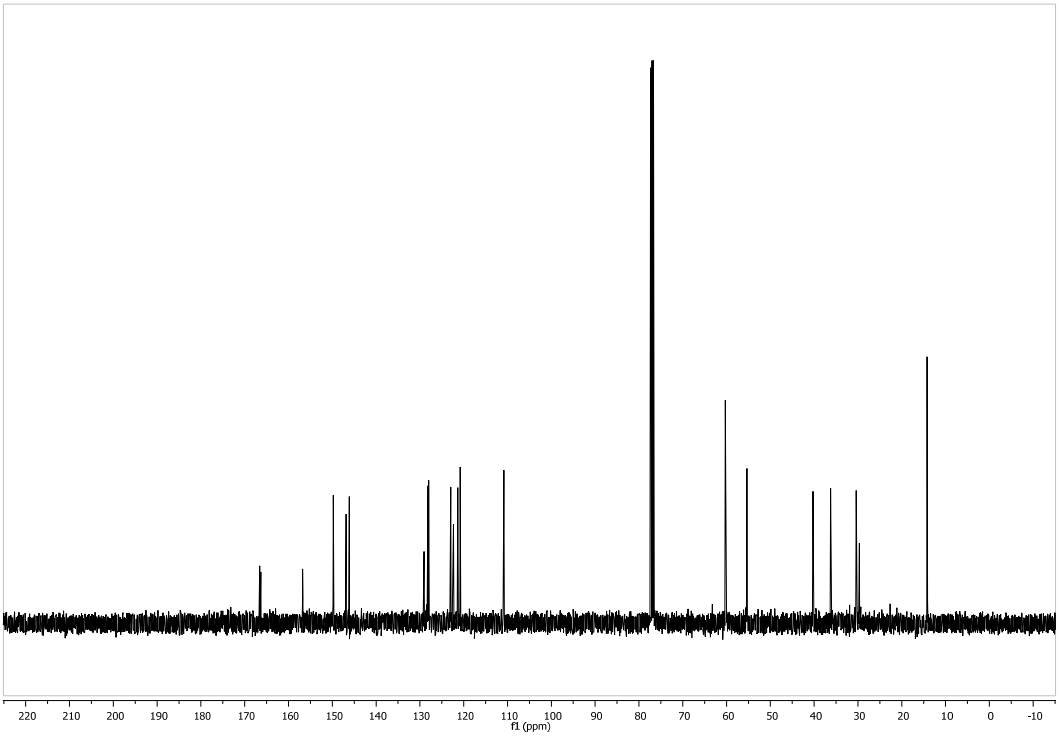
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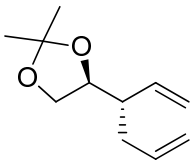

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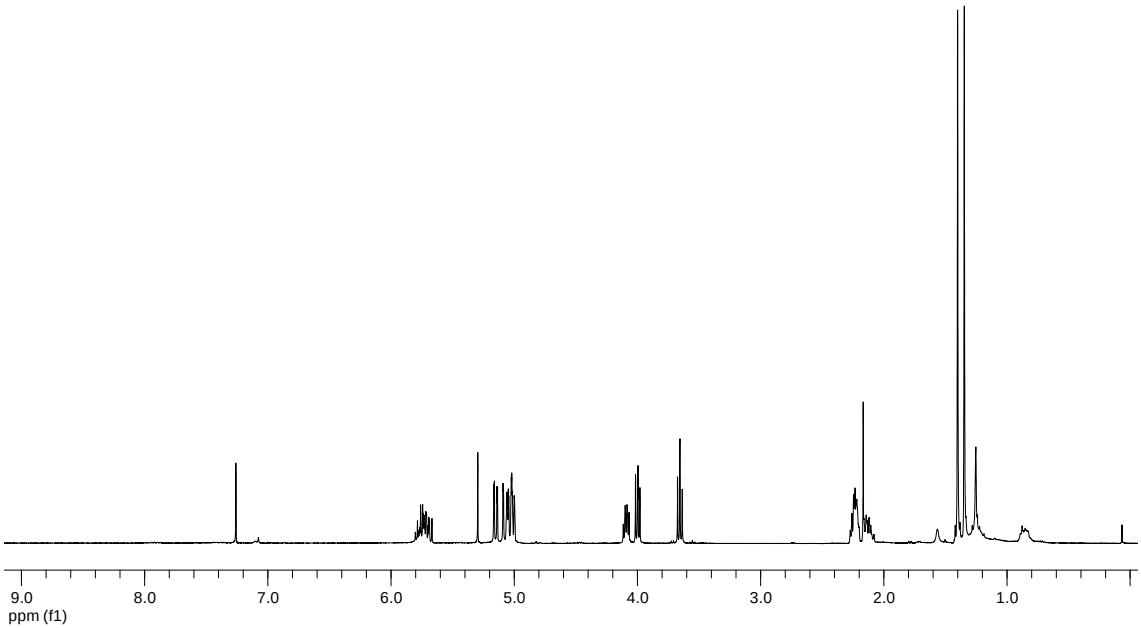

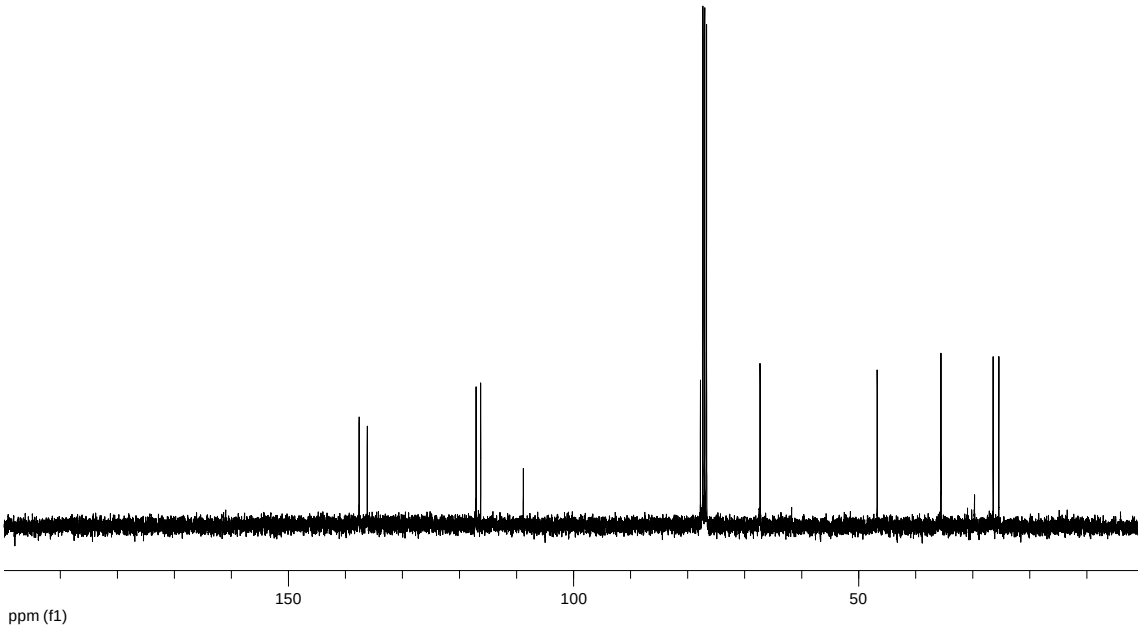

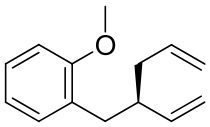

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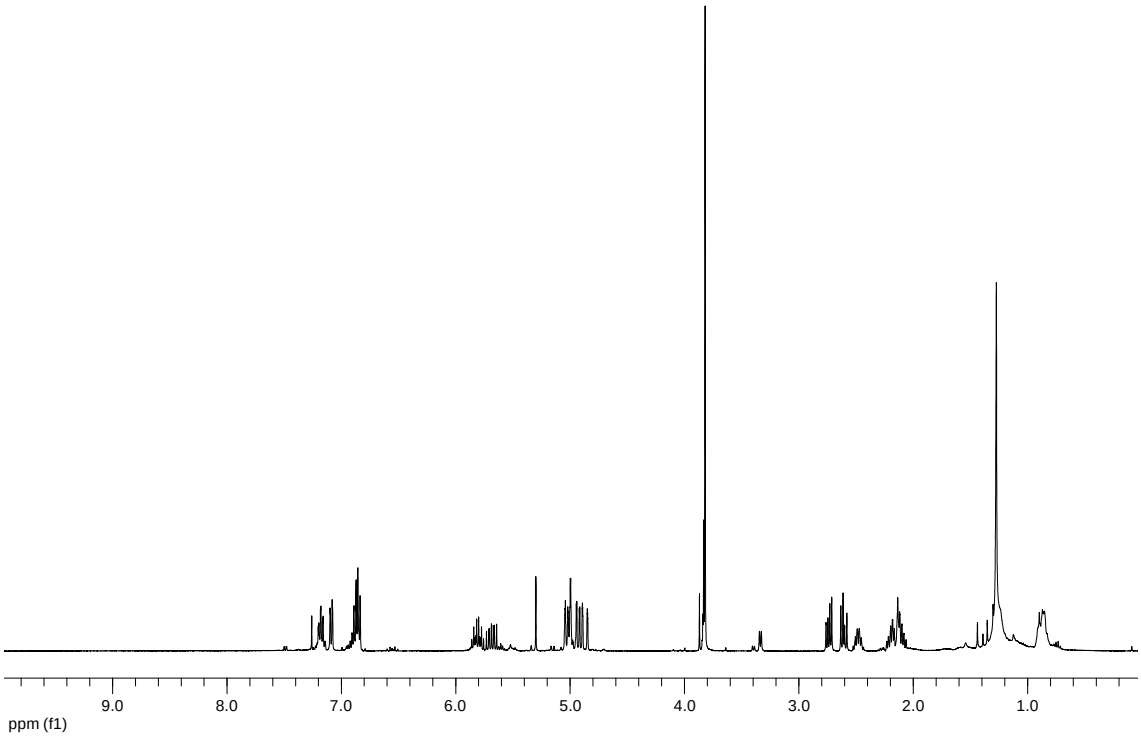

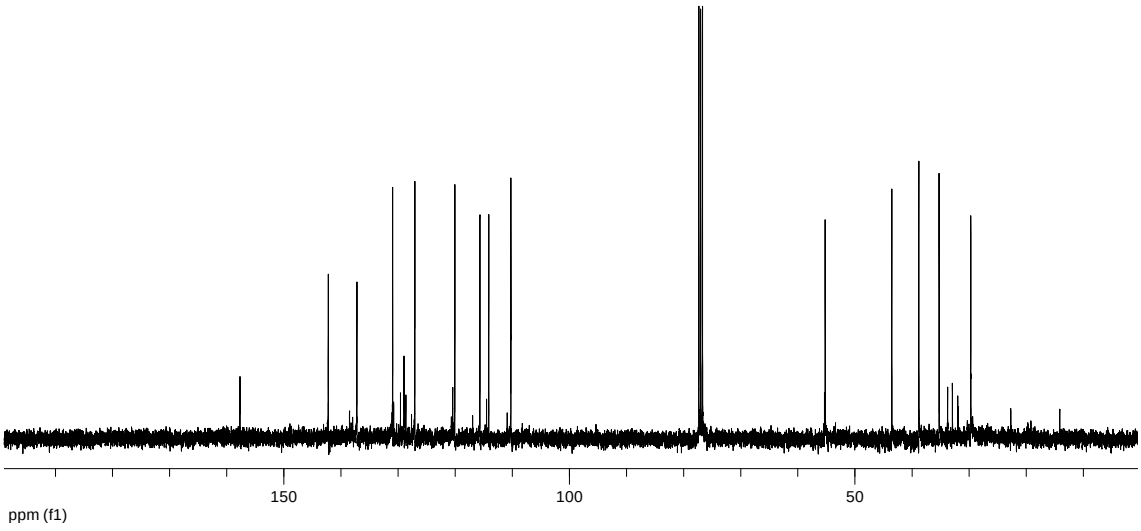

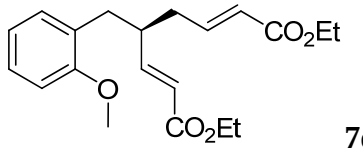
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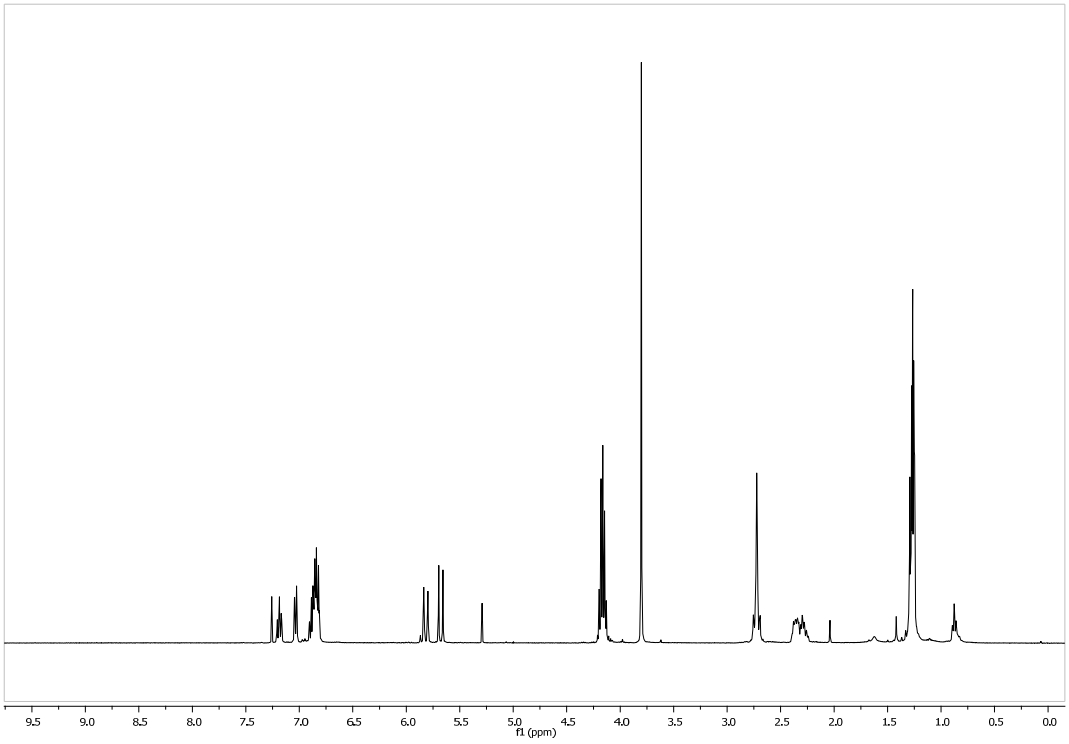
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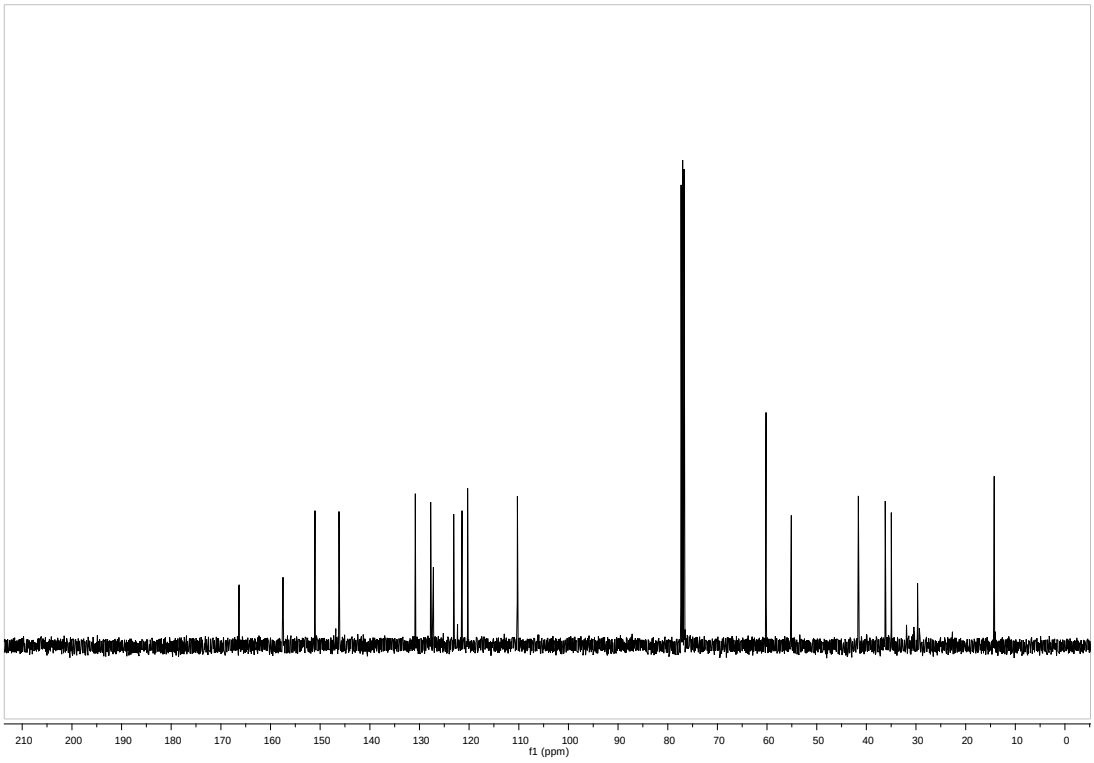
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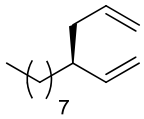

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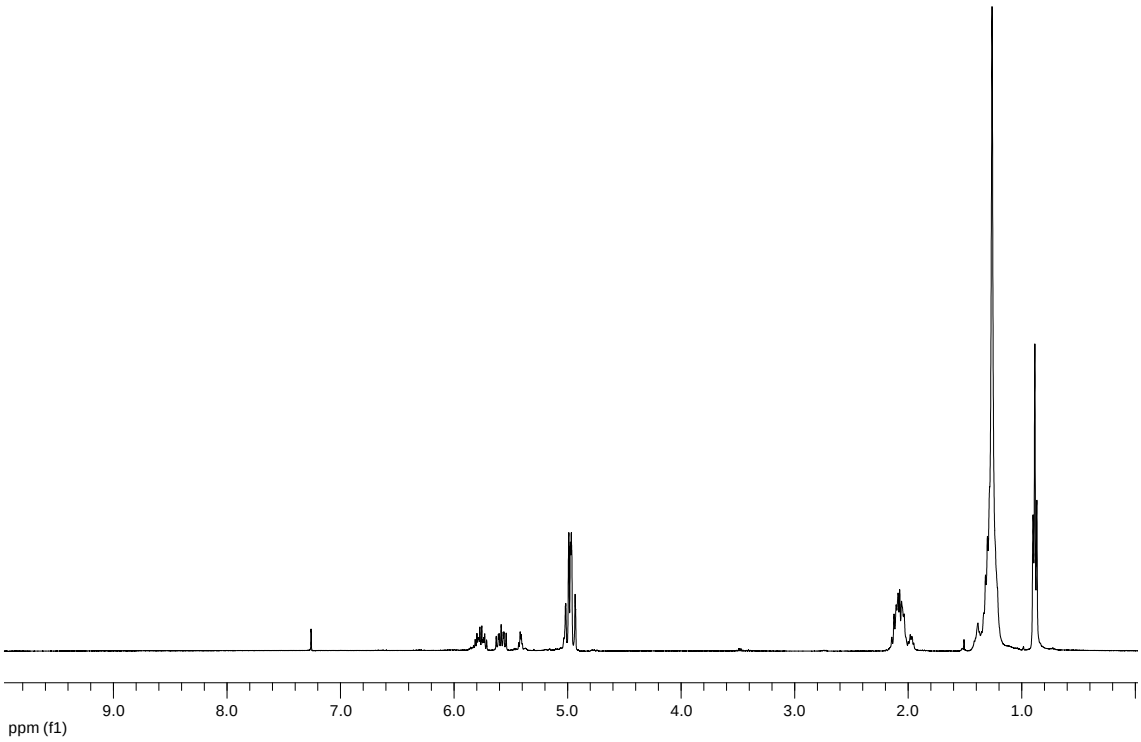

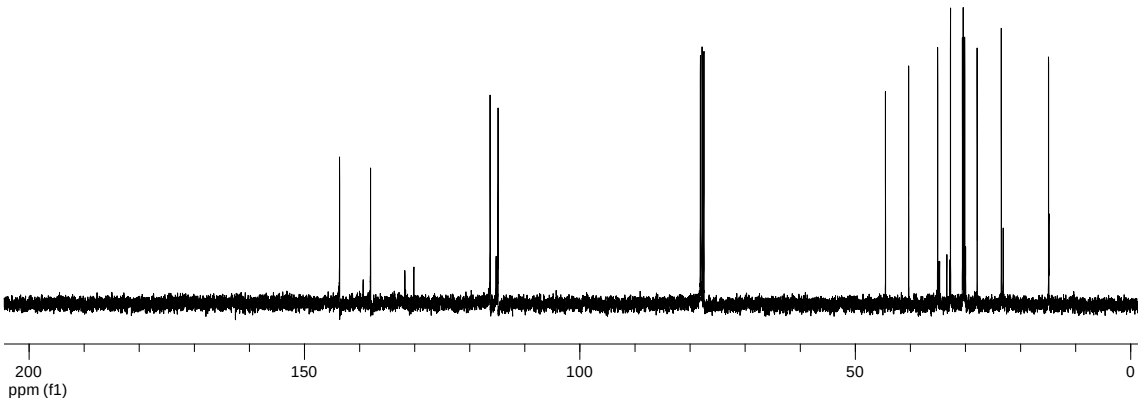

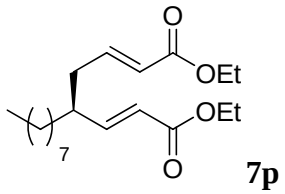

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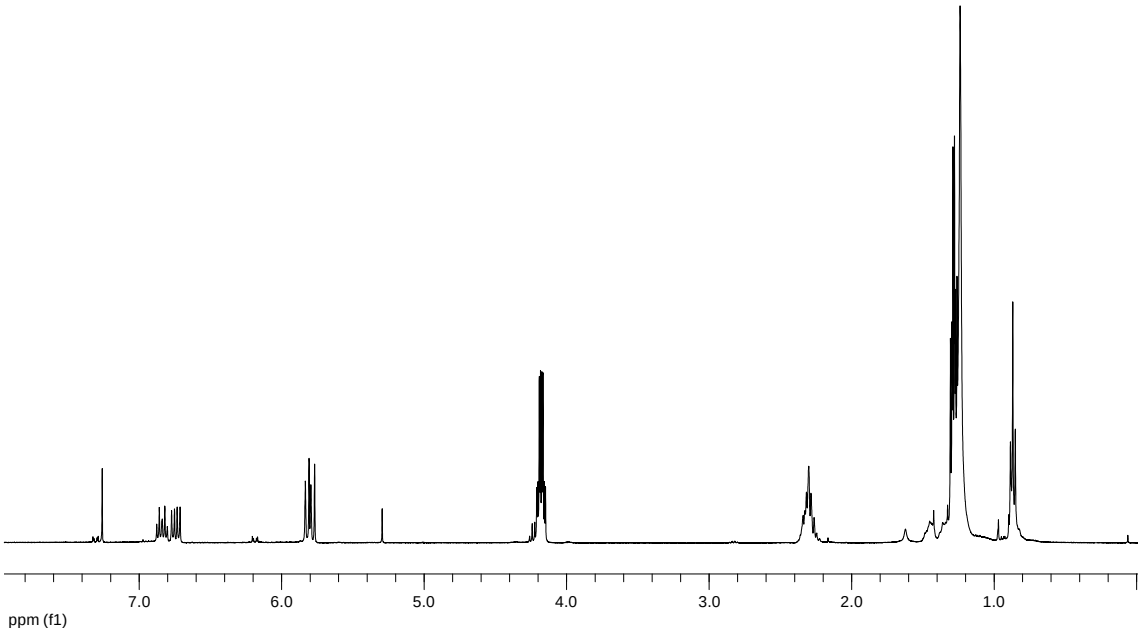

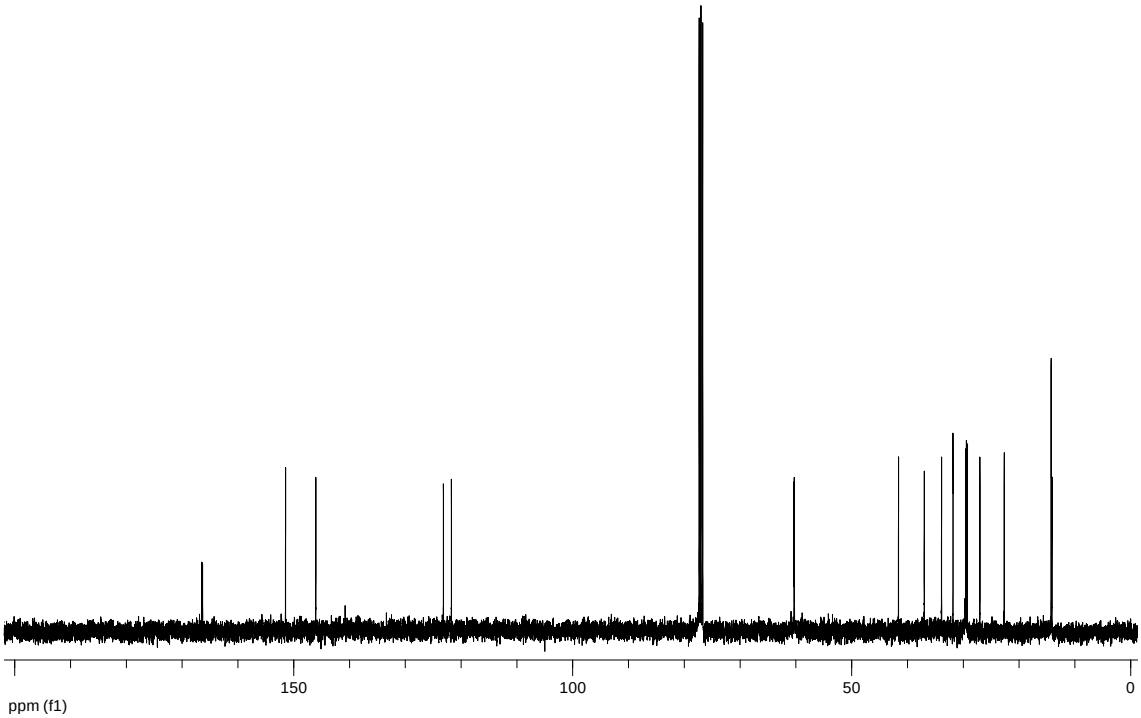

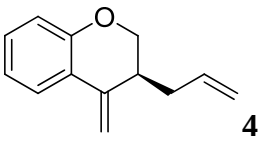

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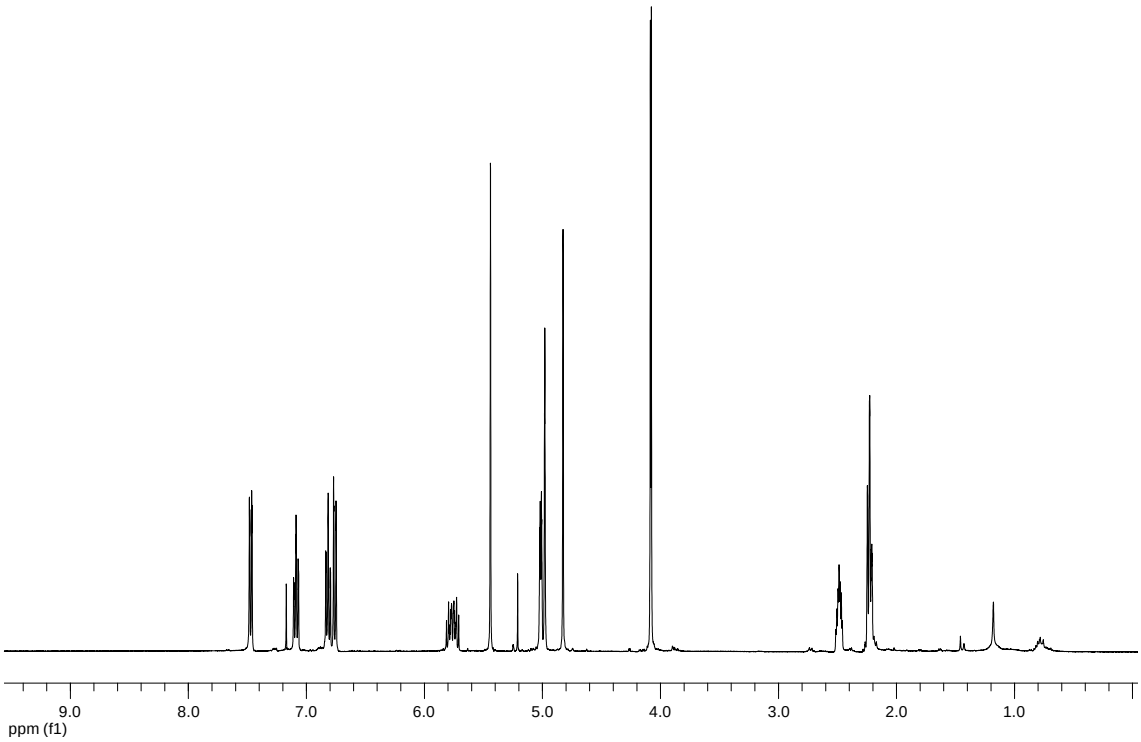

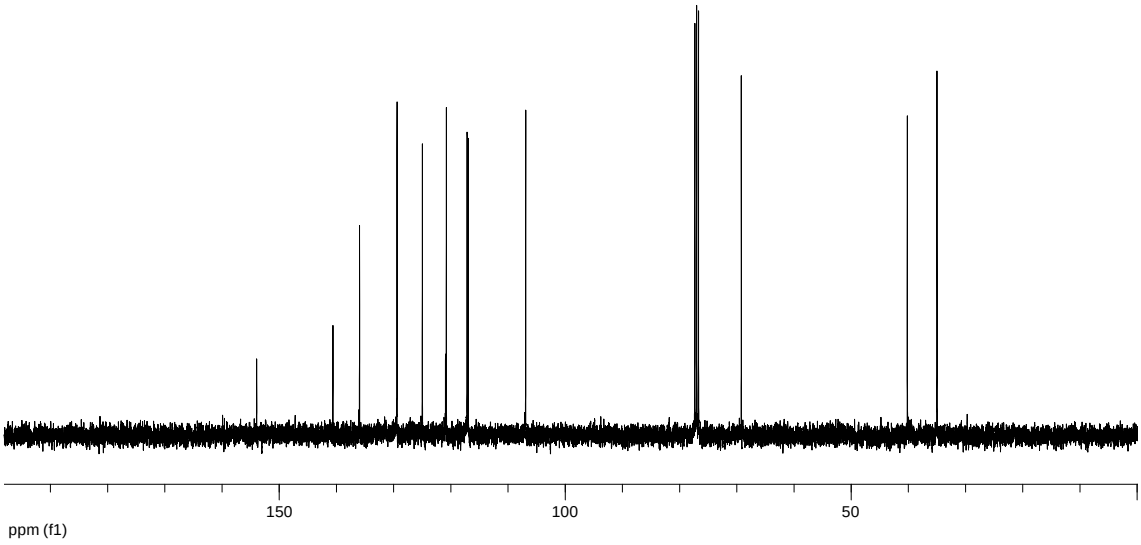

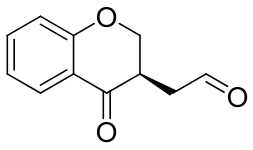

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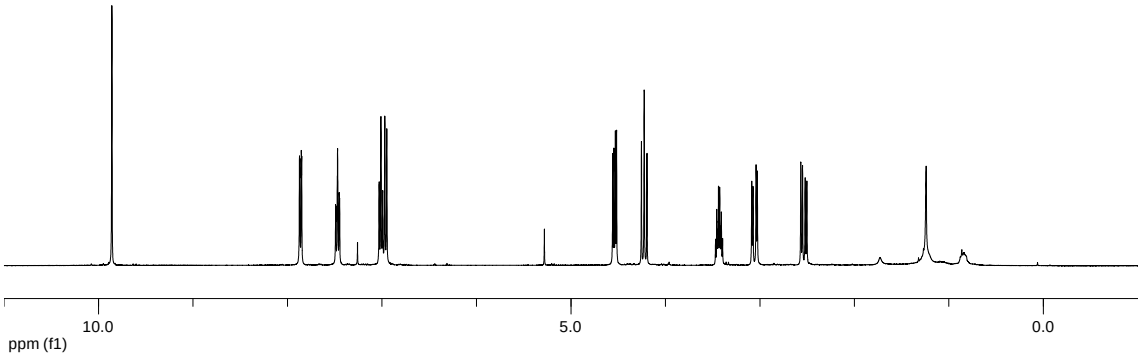

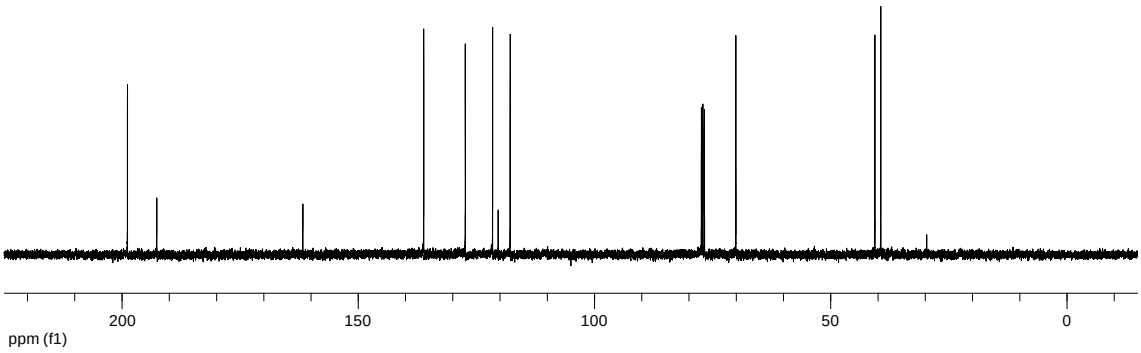

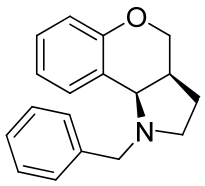

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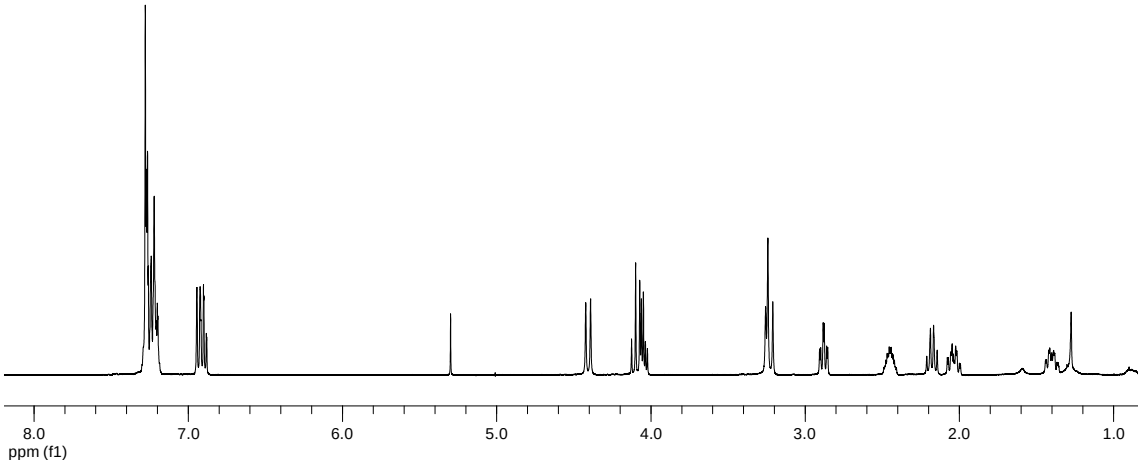
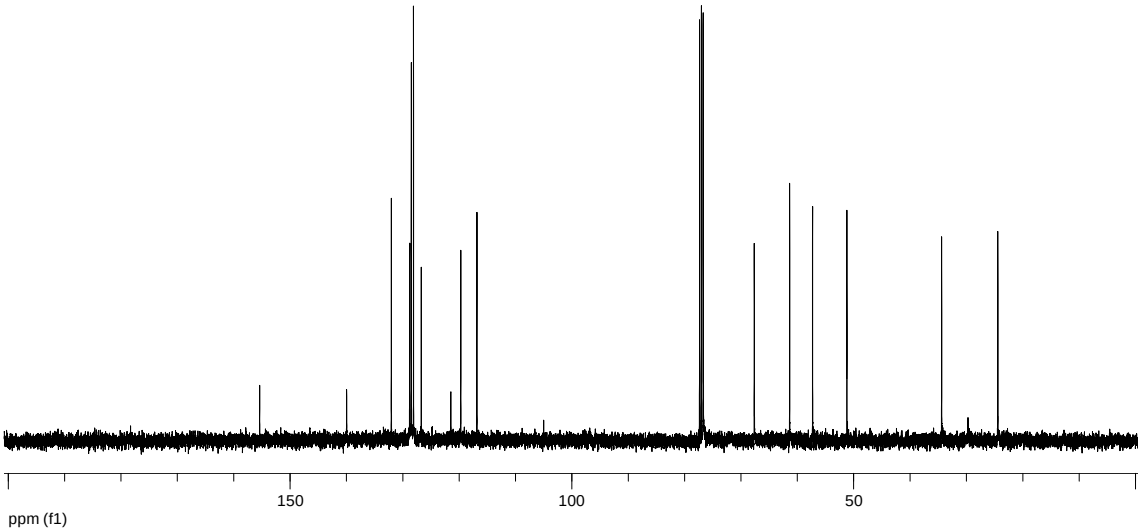
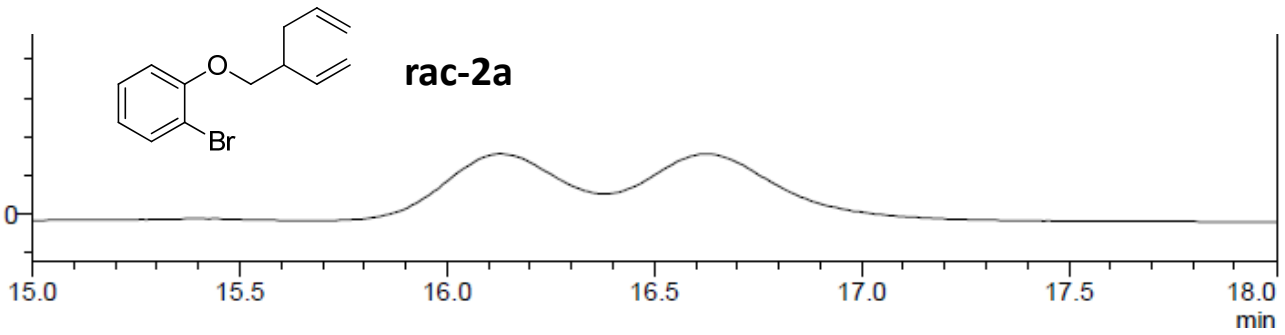
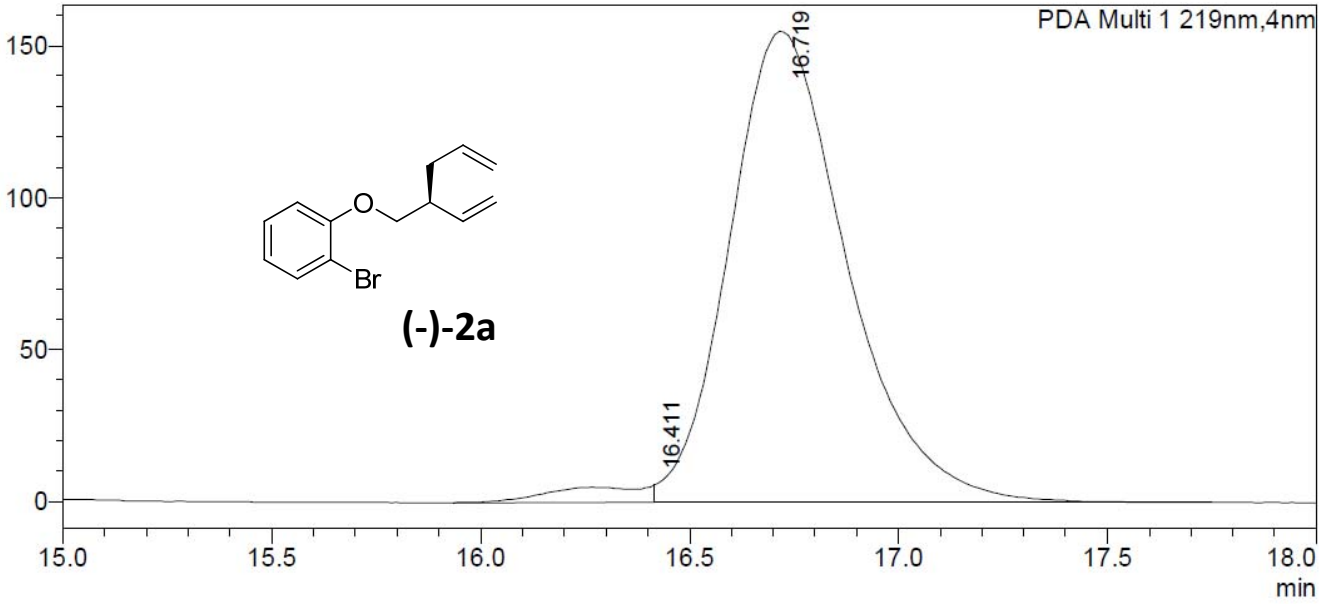


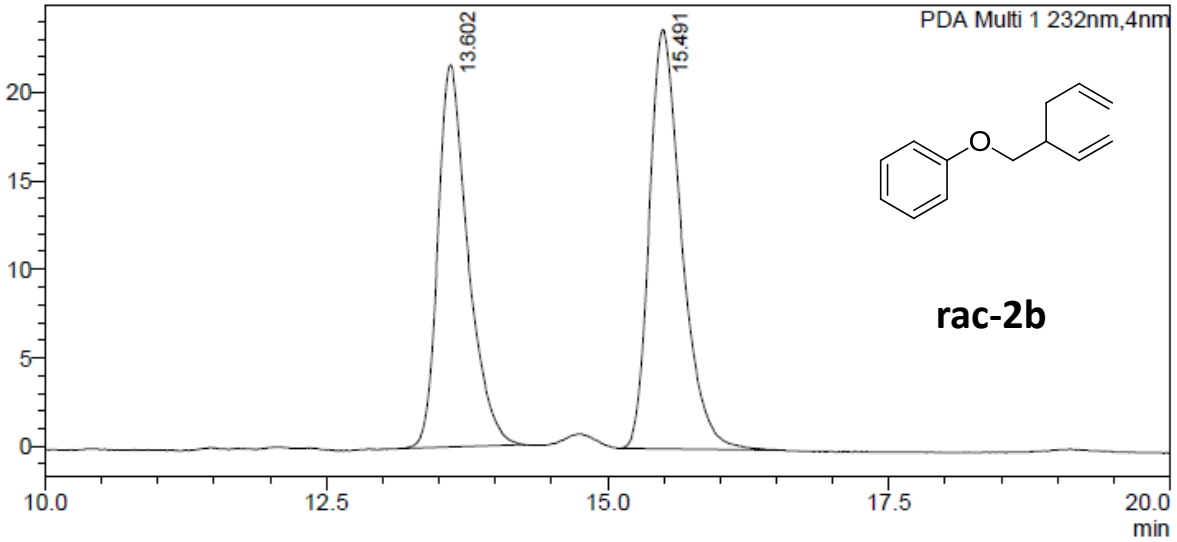


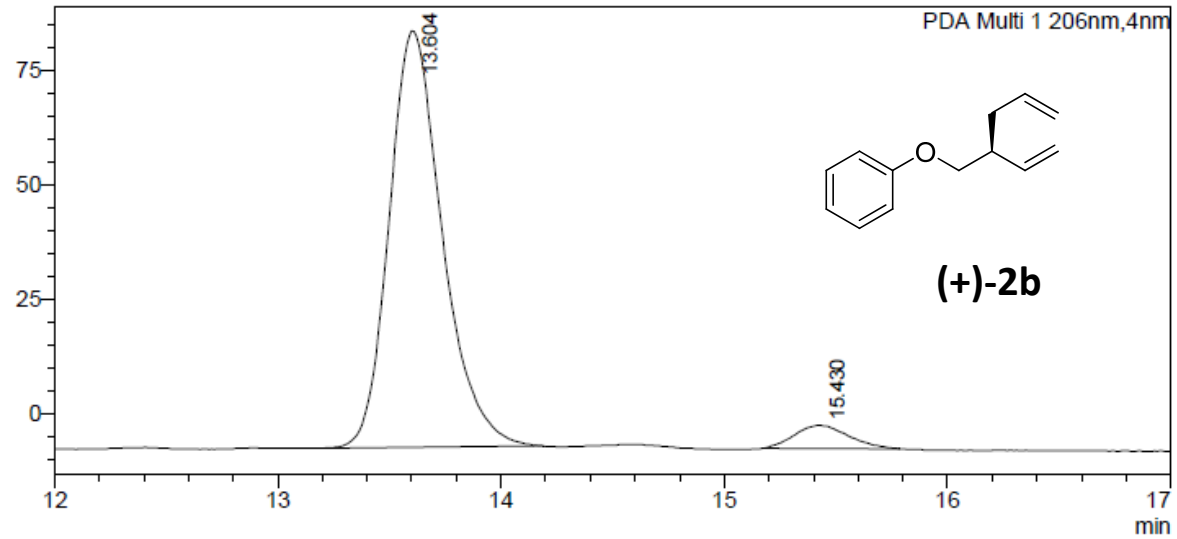
7. Representative HPLC traces:





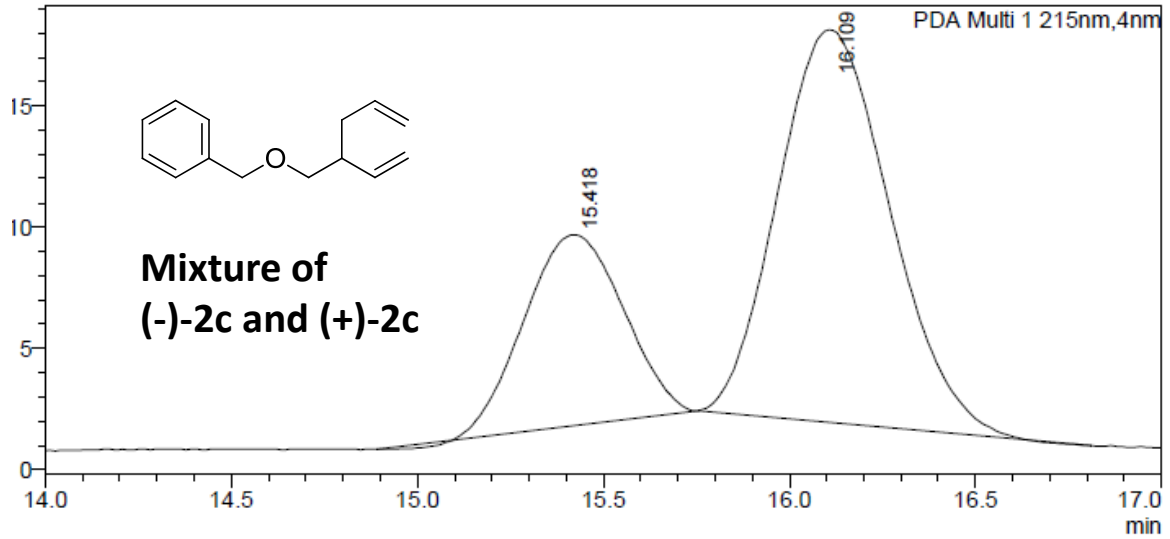
Peak#	Ret. Time	Height	Conc.	Unit	Mark	Name	Area%
1	16.411	5138	0.000		M		2.748
2	16.719	155012	0.000		V M		97.252
Total		160149					100.000

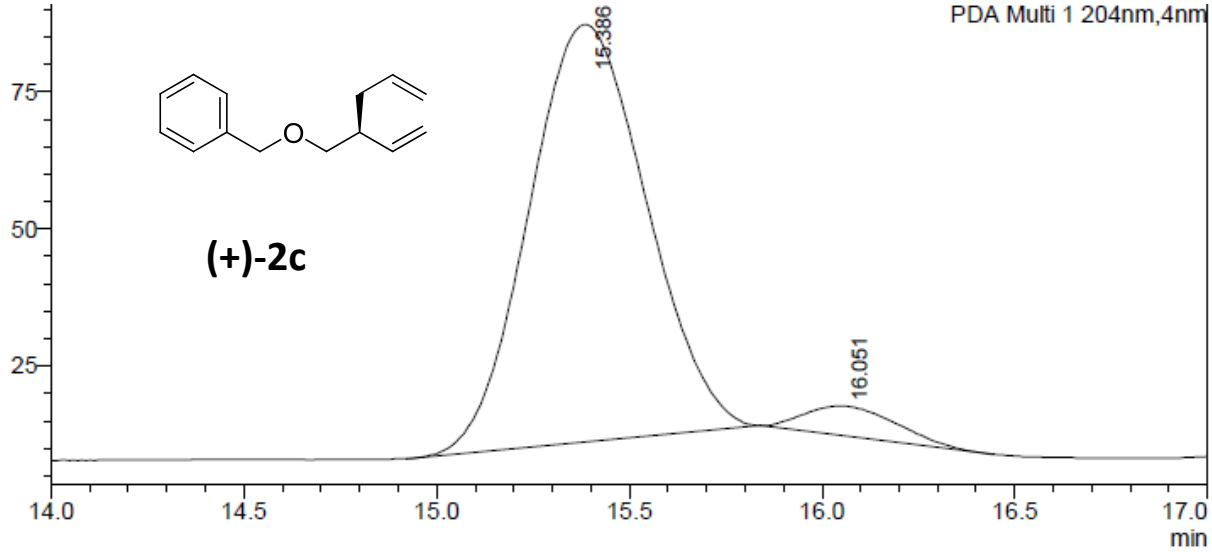




PDA Ch1 206nm

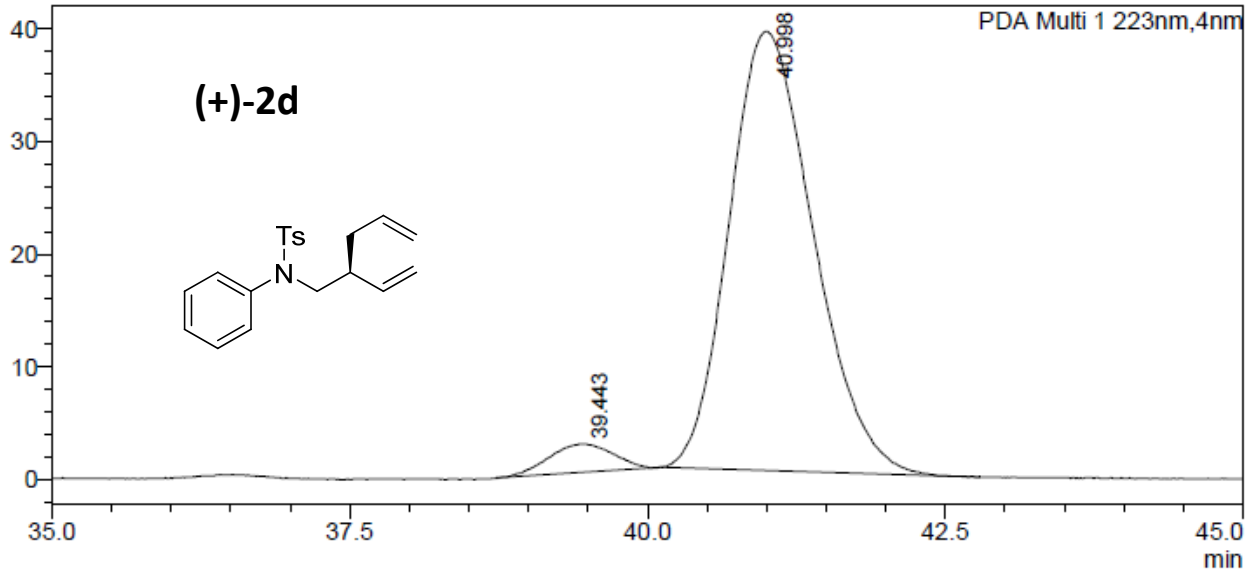
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	13.604	1506955	90904	0.000		M	94.735
2	15.430	83745	4995	0.000		M	5.265
Total		1590700	95900				100.000

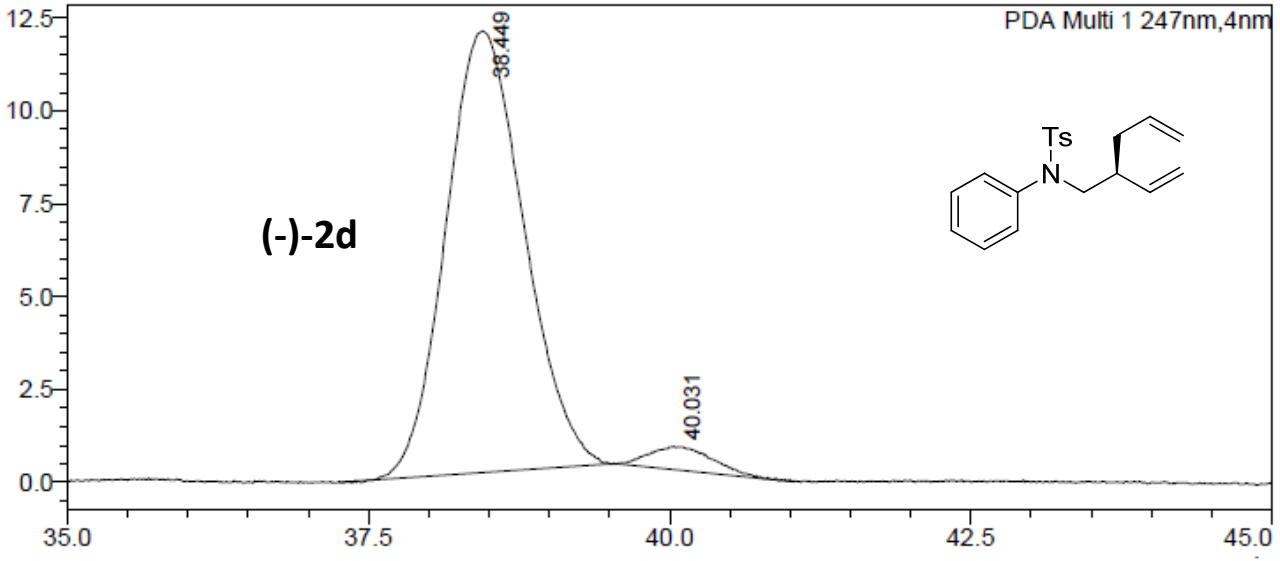




PDA Ch1 204nm

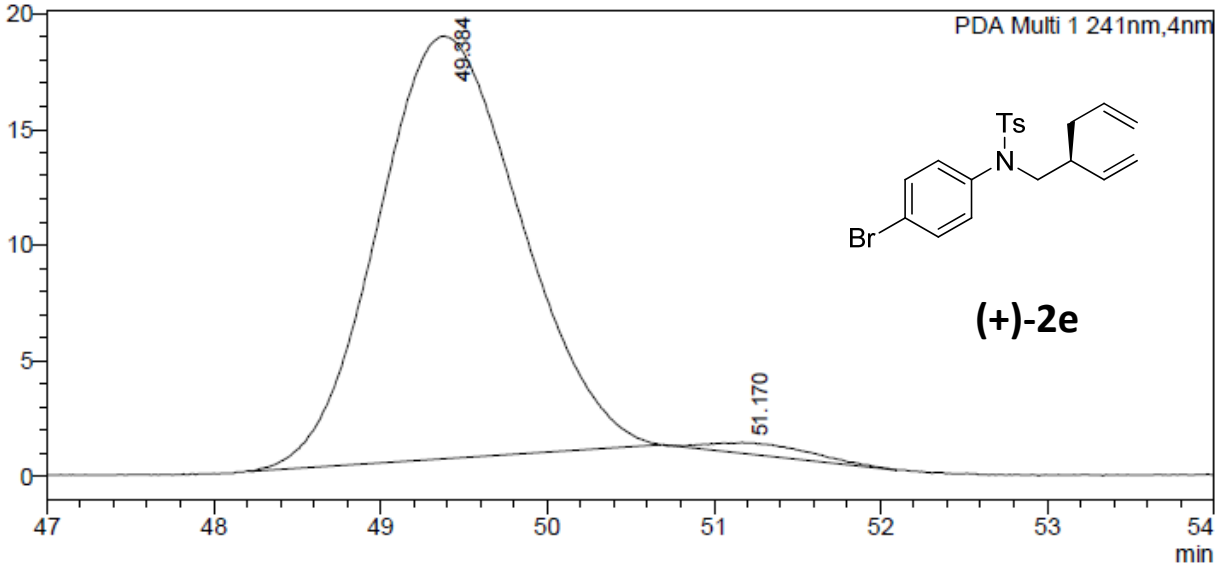
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	15.386	1615056	76120	0.000		M	94.724
2	16.051	89964	5392	0.000		M	5.276
Total		1705020	81511				100.000

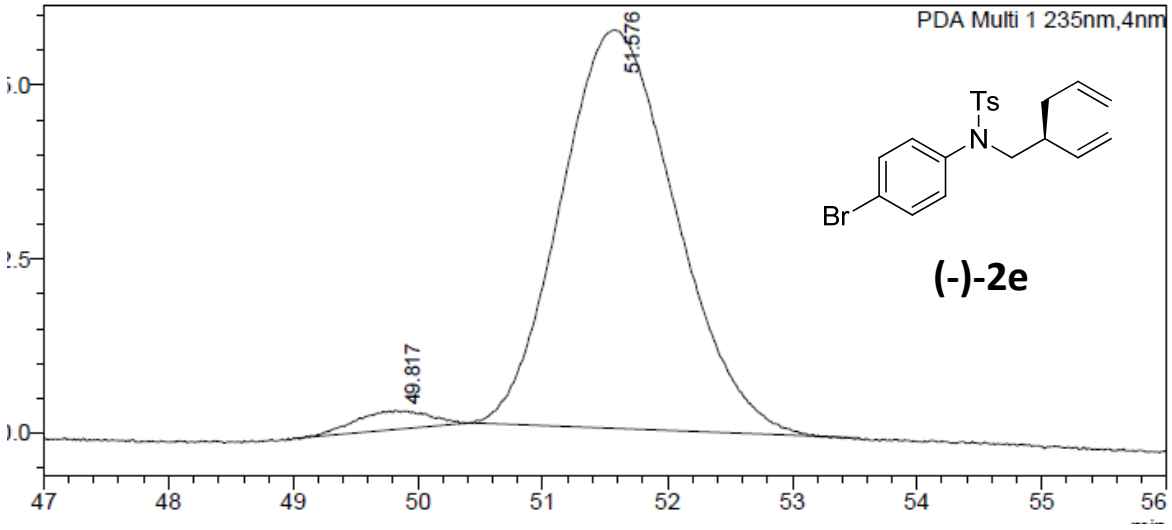




PDA Ch1 247nm

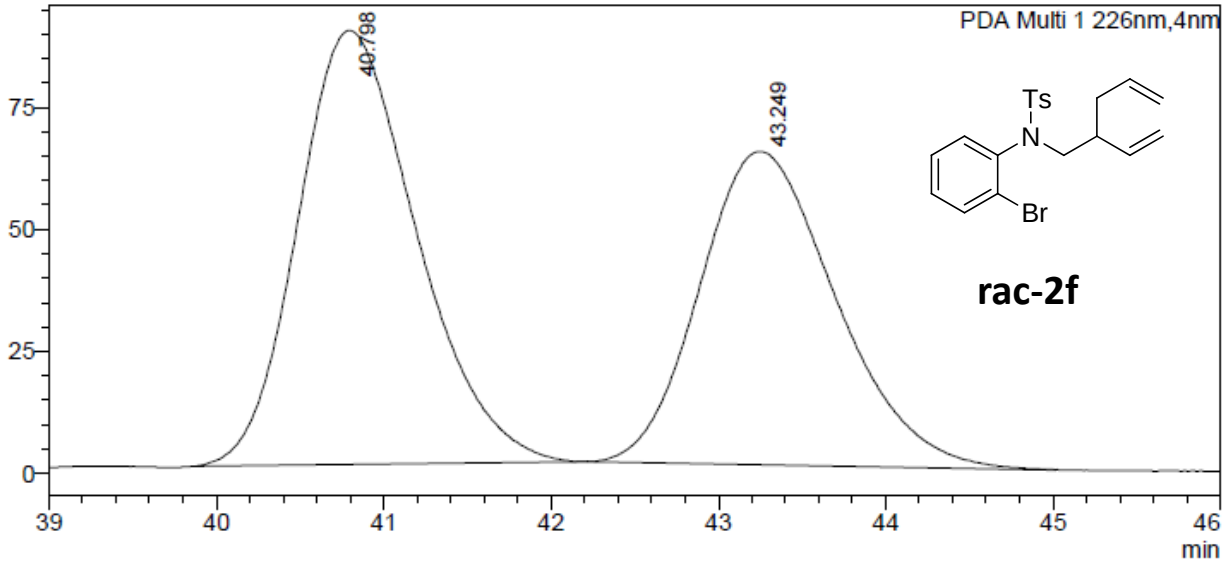
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	38.449	536845	11876	0.000		M	95.829
2	40.031	23364	627	0.000		M	4.171
Total		560209	12503				100.000

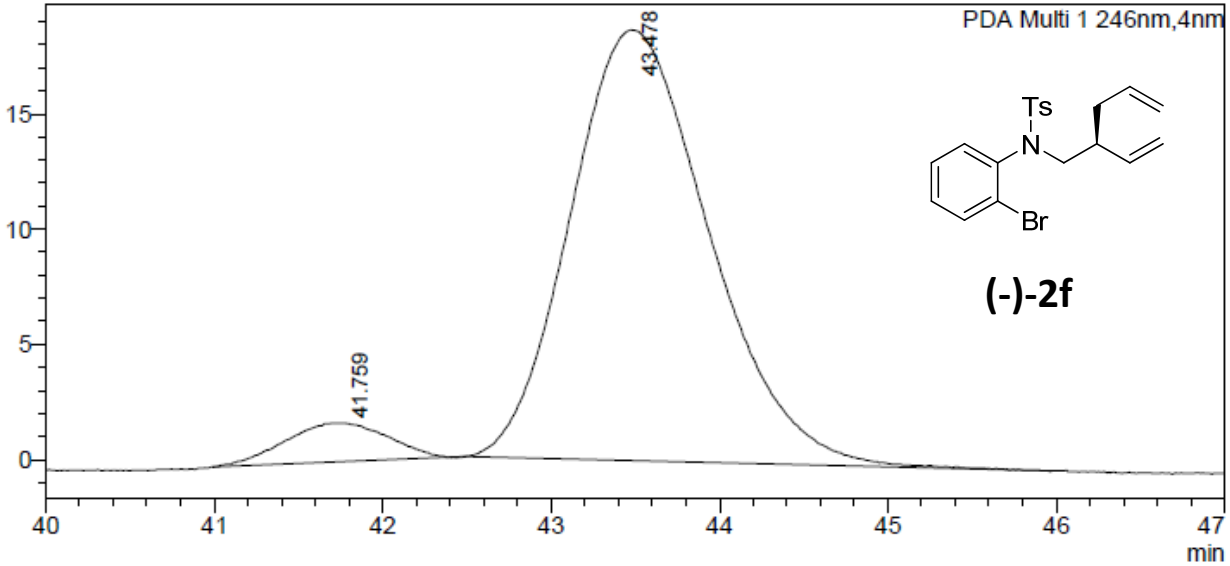




PDA Ch1 235nm

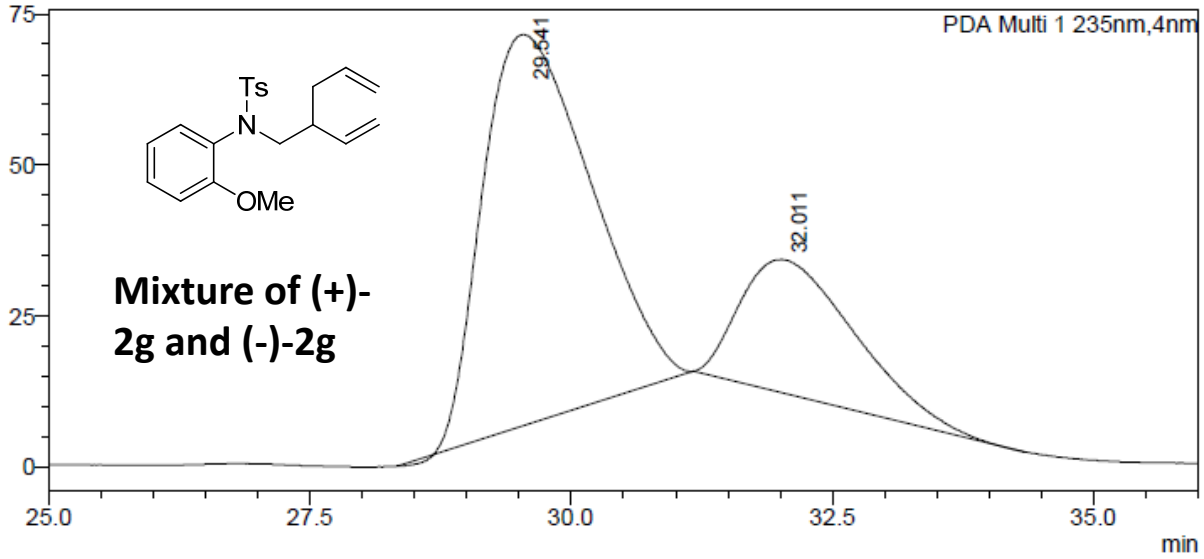
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	49.817	11420	278	0.000		M	3.017
2	51.576	367099	5730	0.000		M	96.983
Total		378519	6008				100.000

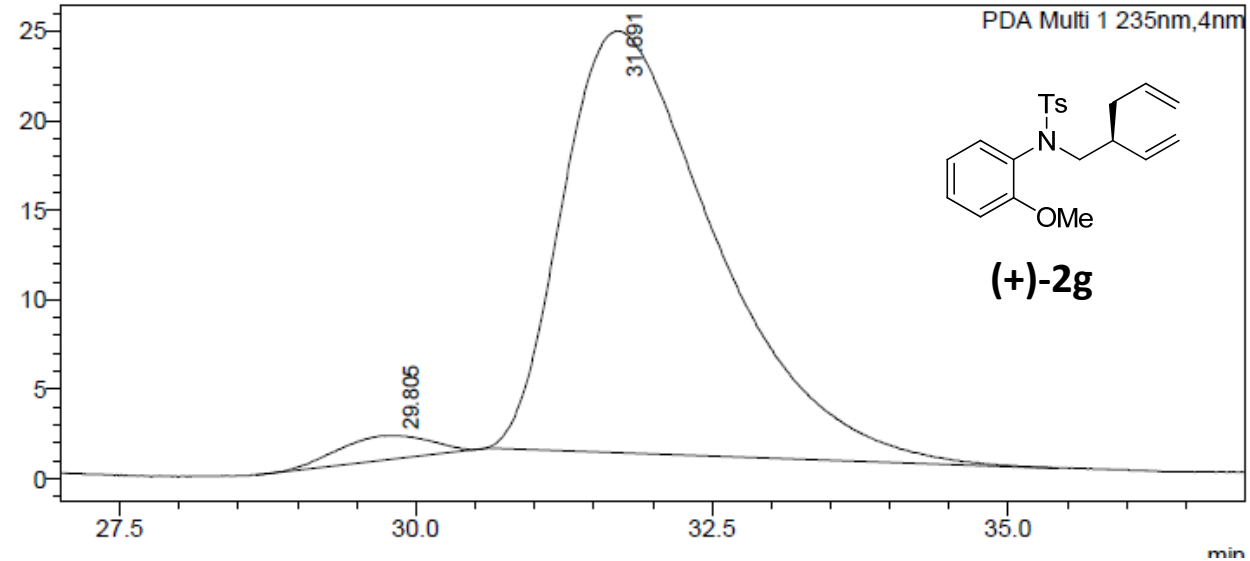




PDA Ch1 246nm

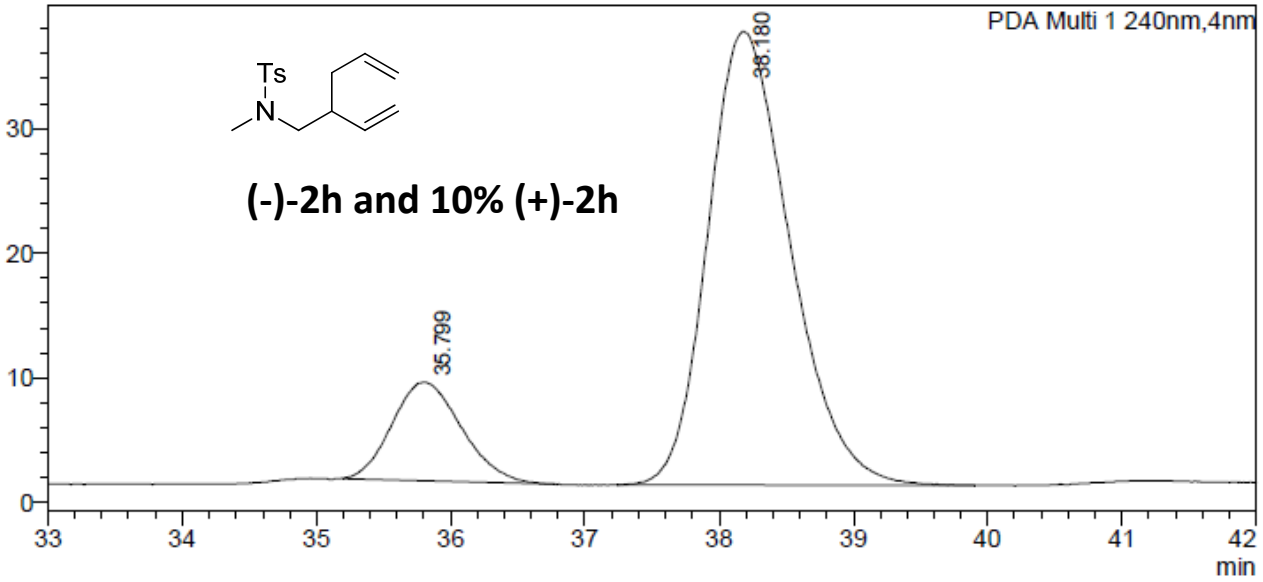
Peak#	Ret. Time	Height	Conc.	Unit	Mark	Area%
1	41.759	1673	6.207		M	6.207
2	43.478	18659	93.793		M	93.793
Total		20332				100.000

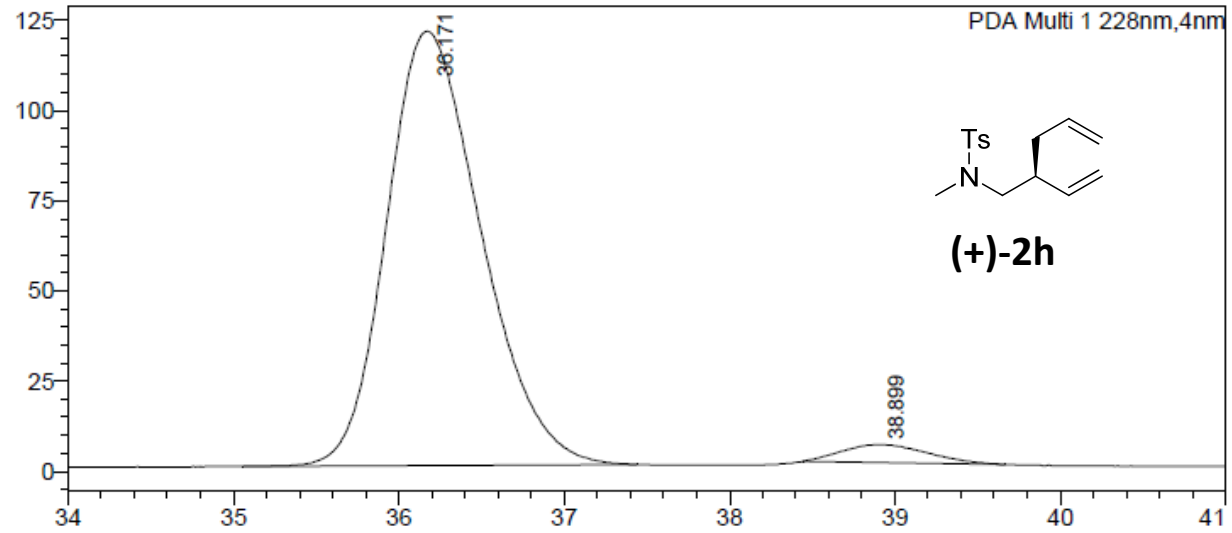




PDA Ch1 235nm

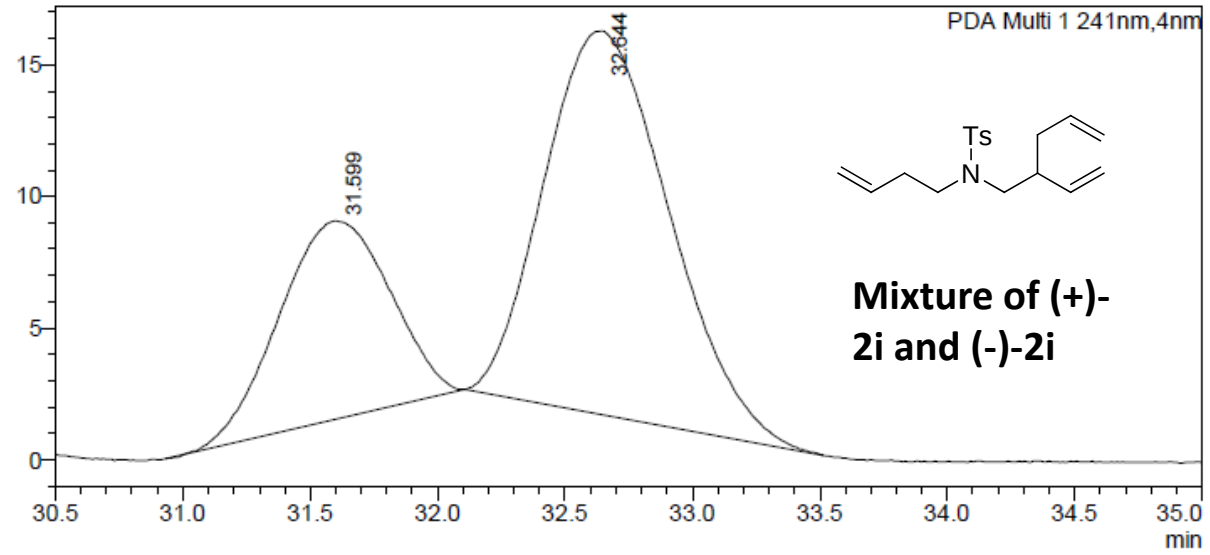
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	29.805	71250	1313	0.000		M	3.247
2	31.691	2123069	23550	0.000		M	96.753
Total		2194319	24863				100.000

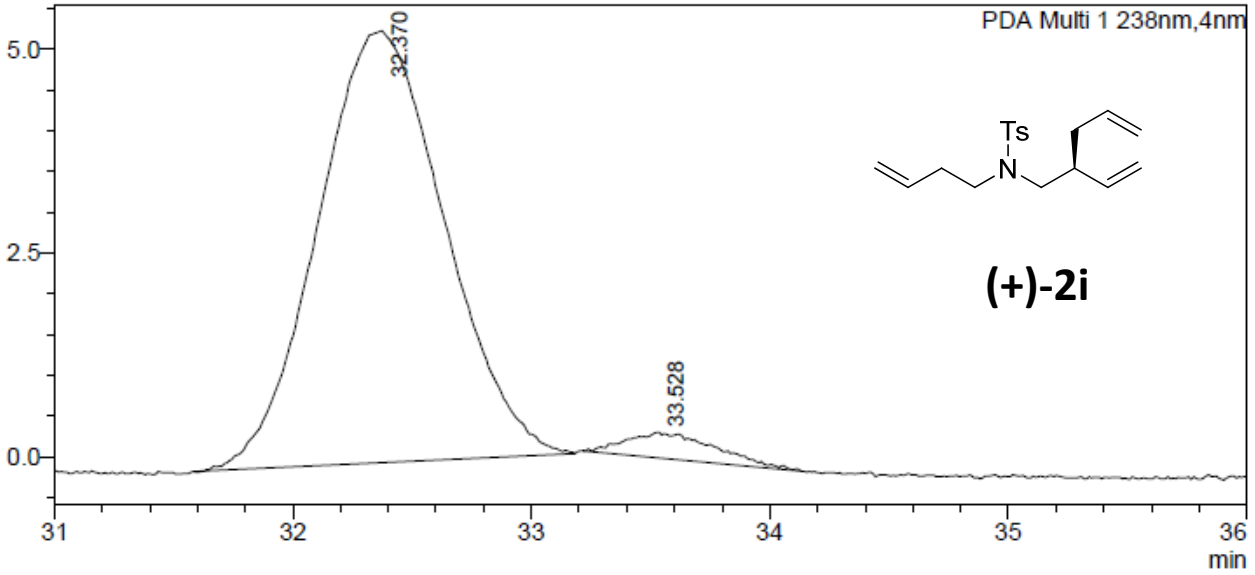




PDA Ch1 228nm

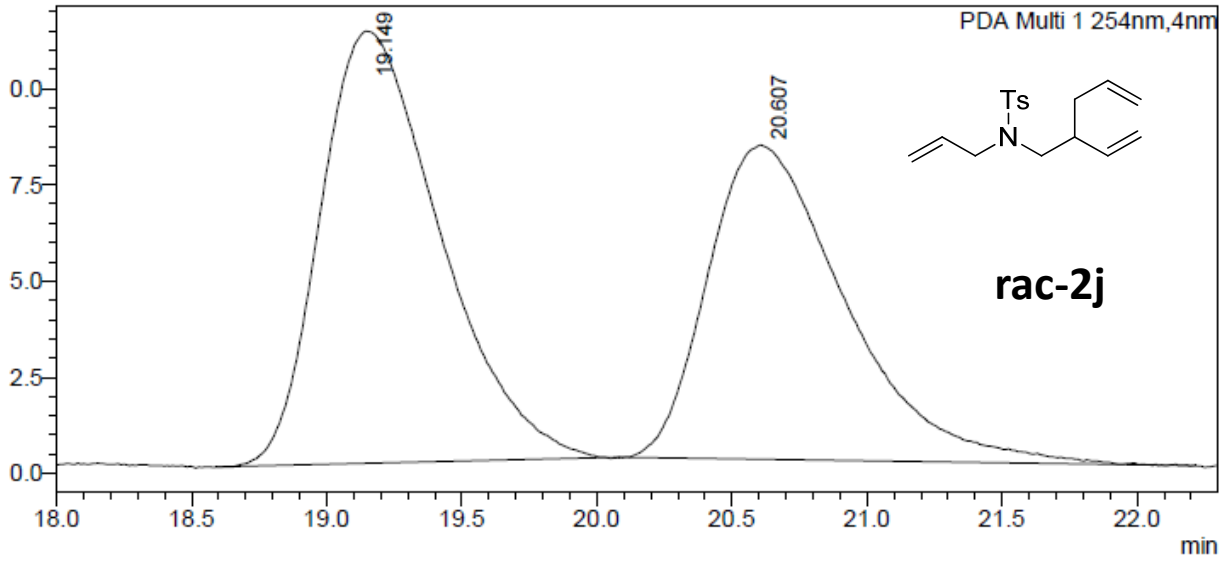
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	36.171	4778180	120253	0.000		M	96.392
2	38.899	178842	4937	0.000		M	3.608
Total		4957023	125190				100.000

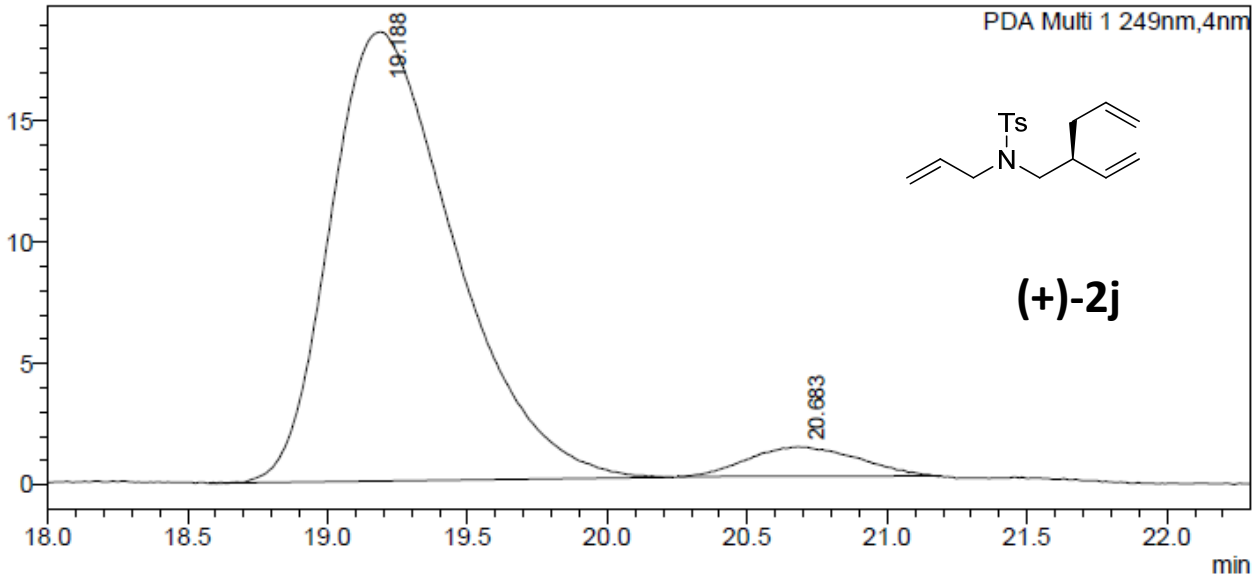




PDA Ch1 238nm

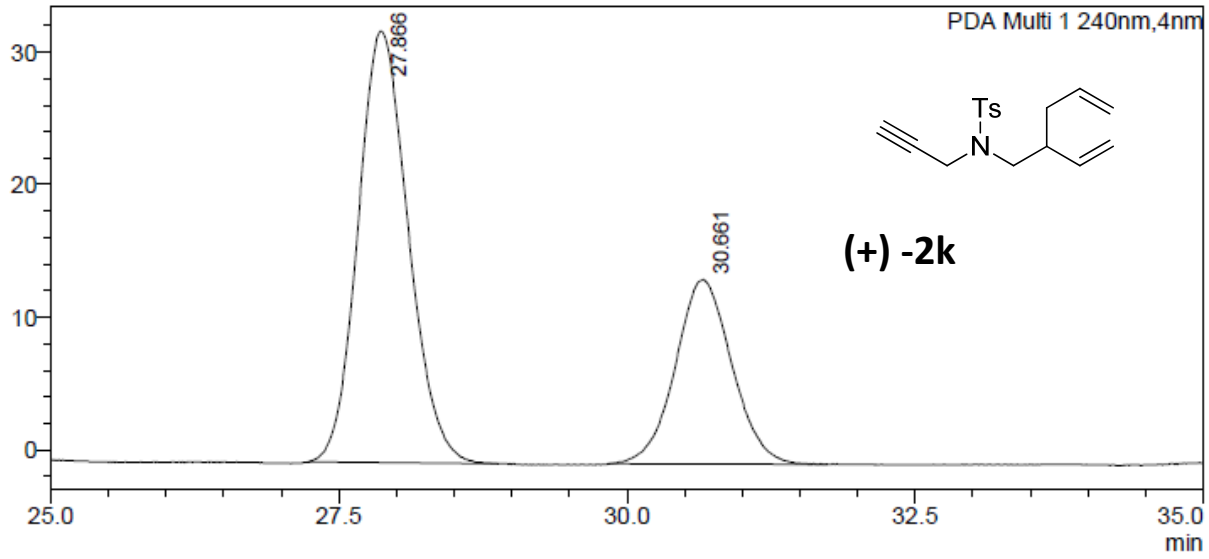
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	32.370	195212	5298	0.000		M	95.815
2	33.528	8527	316	0.000		M	4.185
Total		203739	5615				100.000

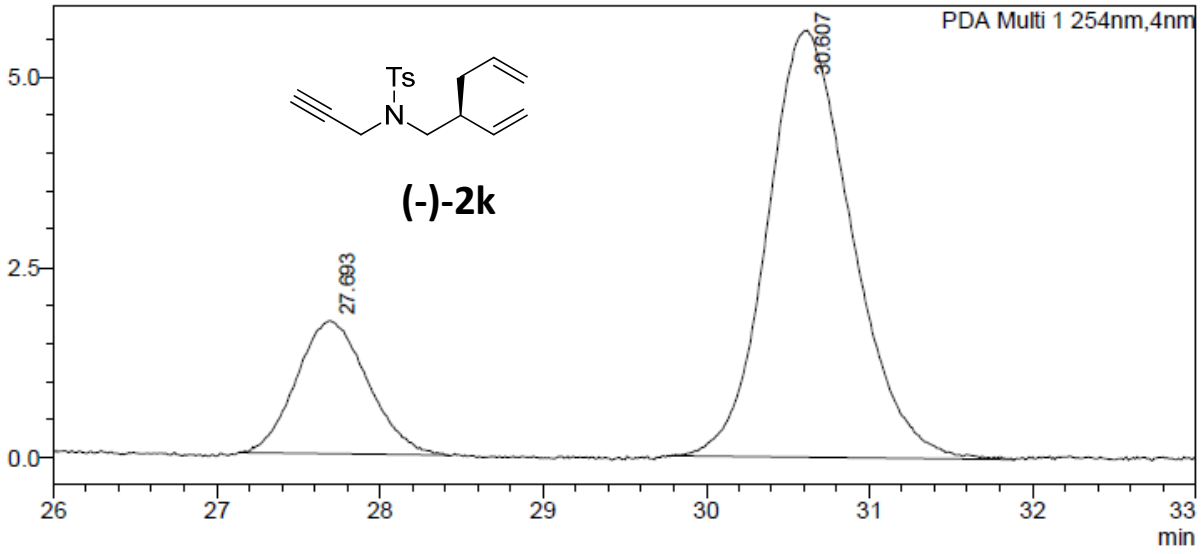




PDA Ch1 249nm

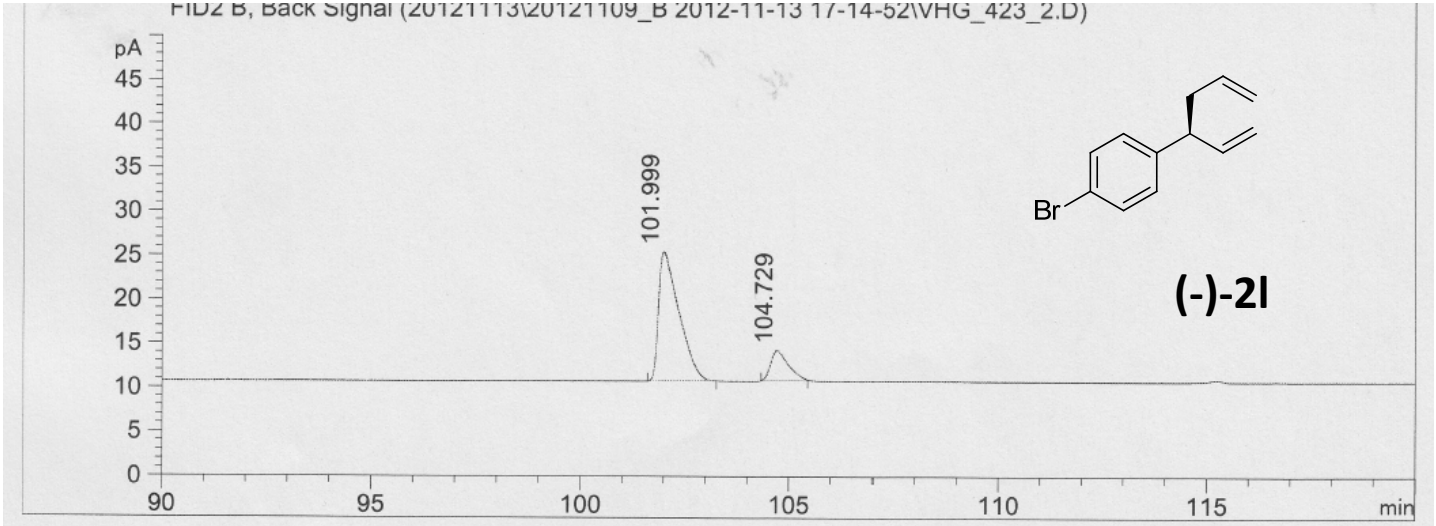
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	19.188	572065	18522	0.000		M	94.431
2	20.683	33736	1228	0.000		M	5.569
Total		605801	19750				100.000

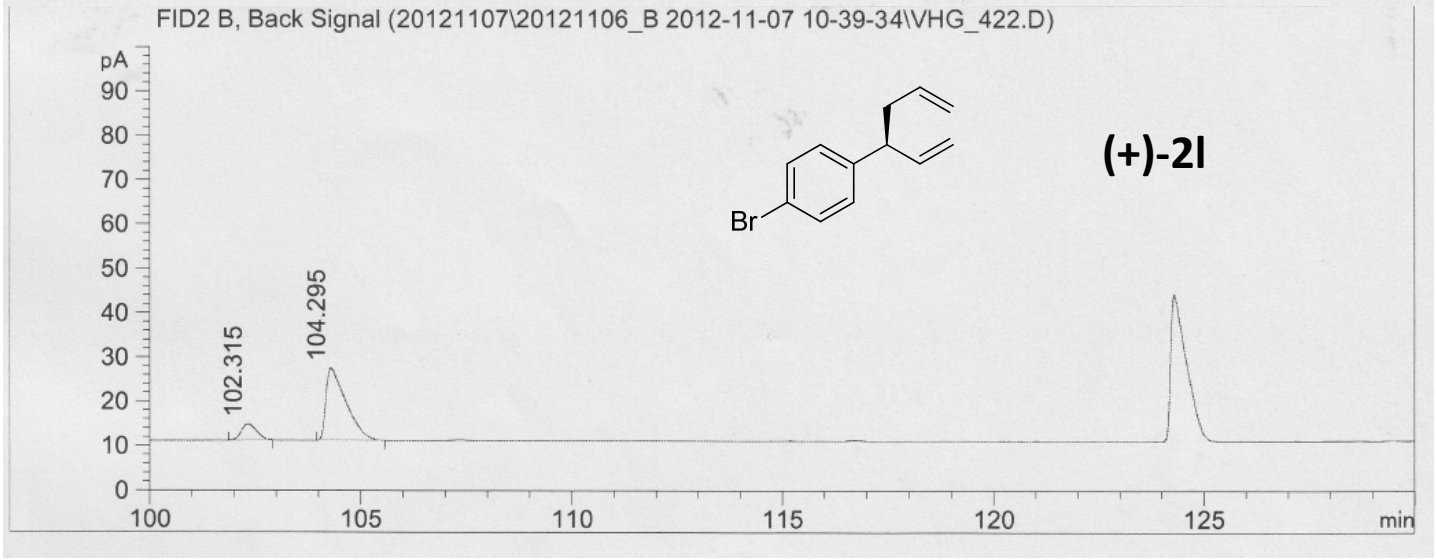




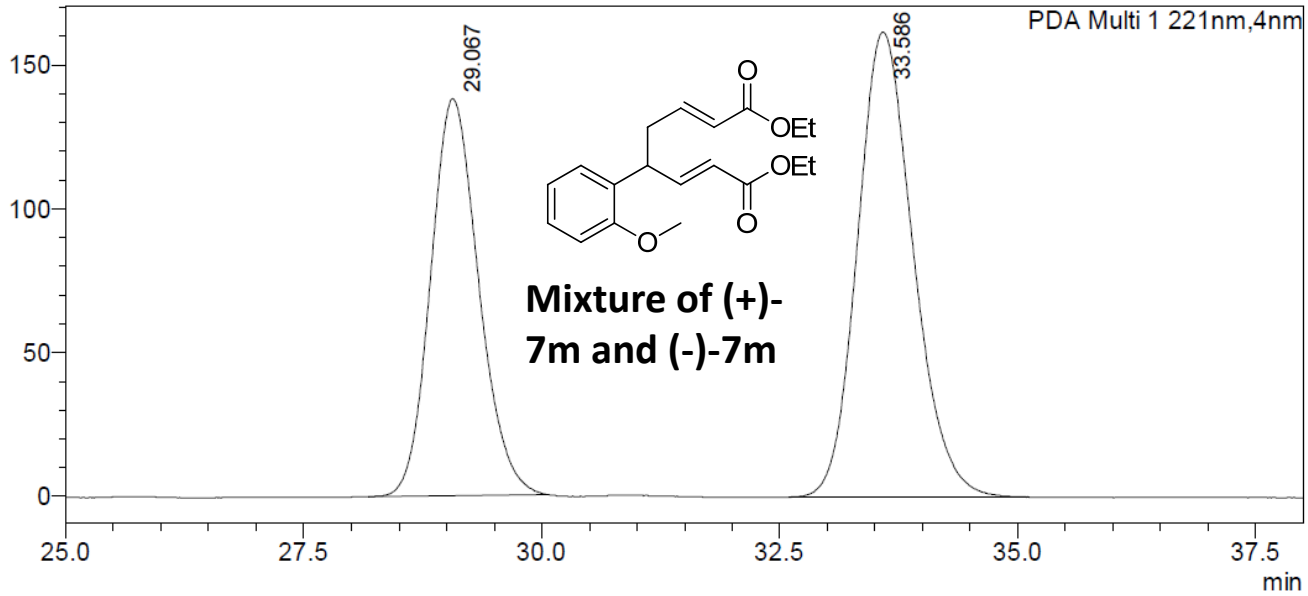
PDA Ch1 254nm

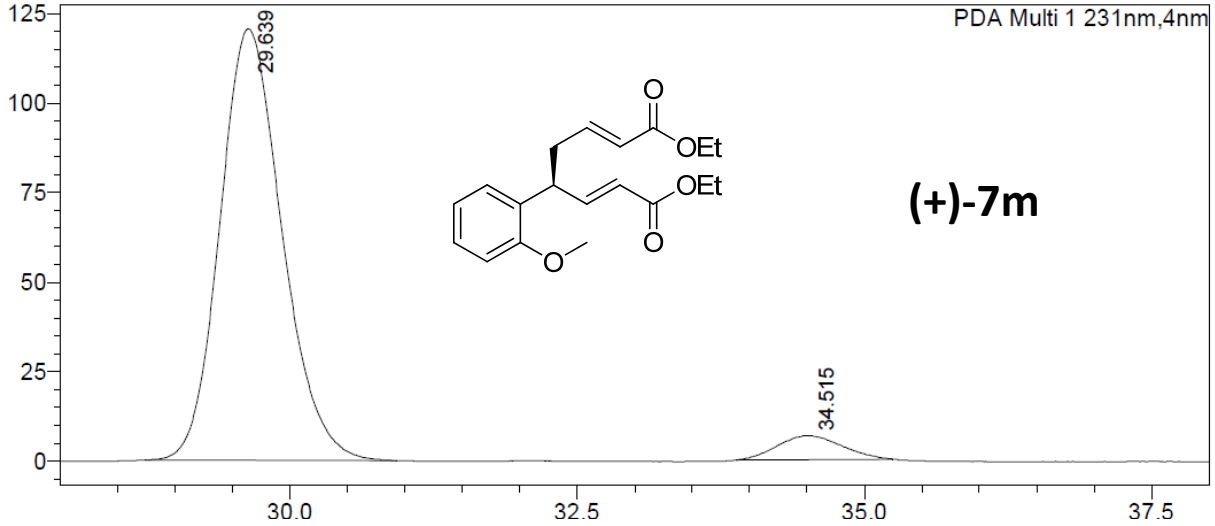
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	27.693	53011	1749	0.000		M	20.822
2	30.607	201574	5611	0.000		M	79.178
Total		254585	7360				100.000





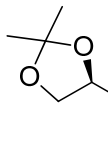
#	Meas.RT	Main Pe	Exp.RT	Resp.%
1	0.000	0.000	12.410	0.000
2	102.315	14.102	0.000	14.102
3	104.295	85.898	0.000	85.898



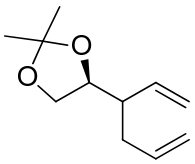


PDA Ch1 231nm

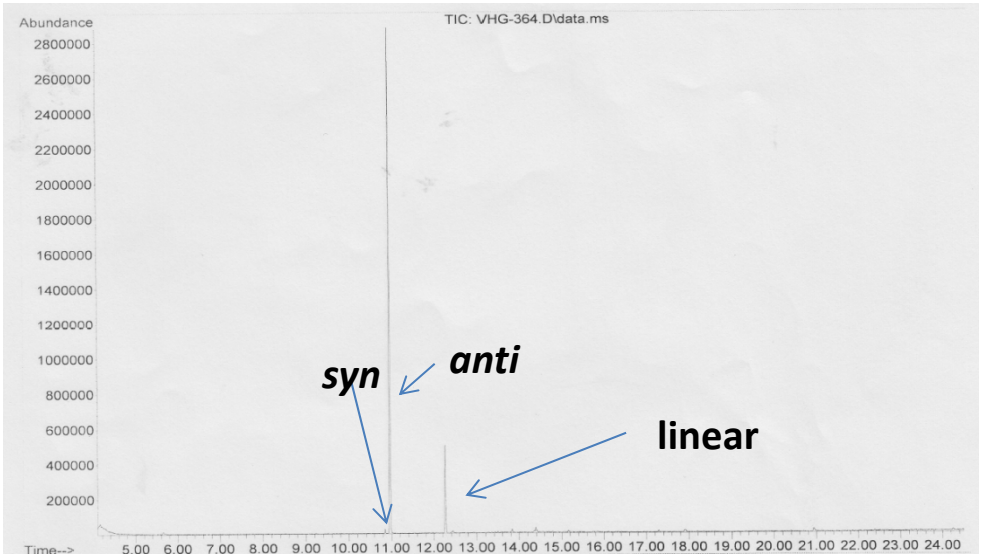
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	29.639	4533016	120493	0.000		M	94.570
2	34.515	260256	6660	0.000		M	5.430
Total		4793271	127153				100.000

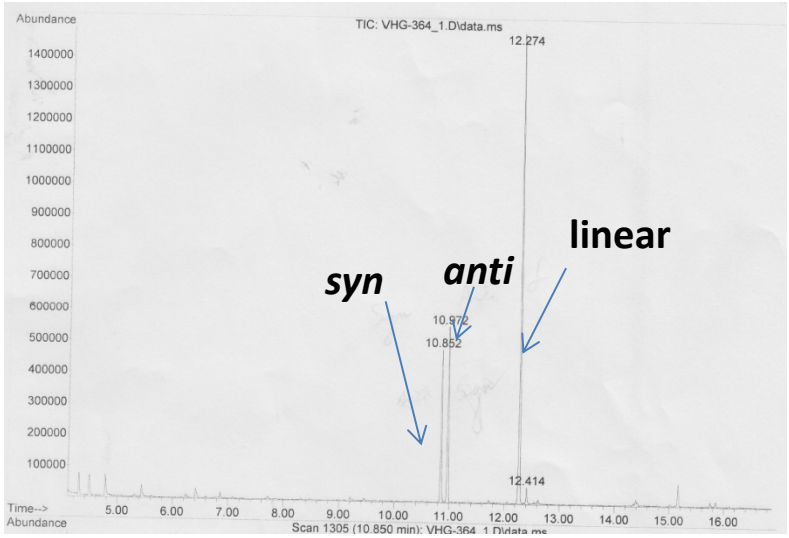


(+)-7m

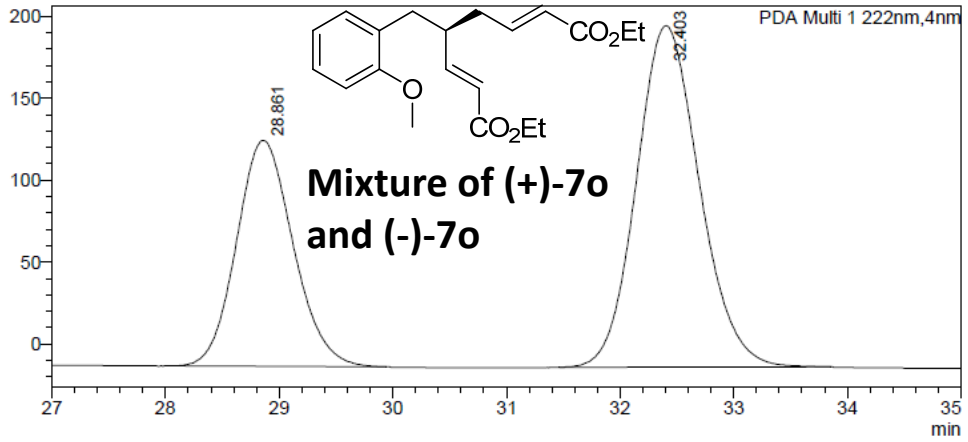


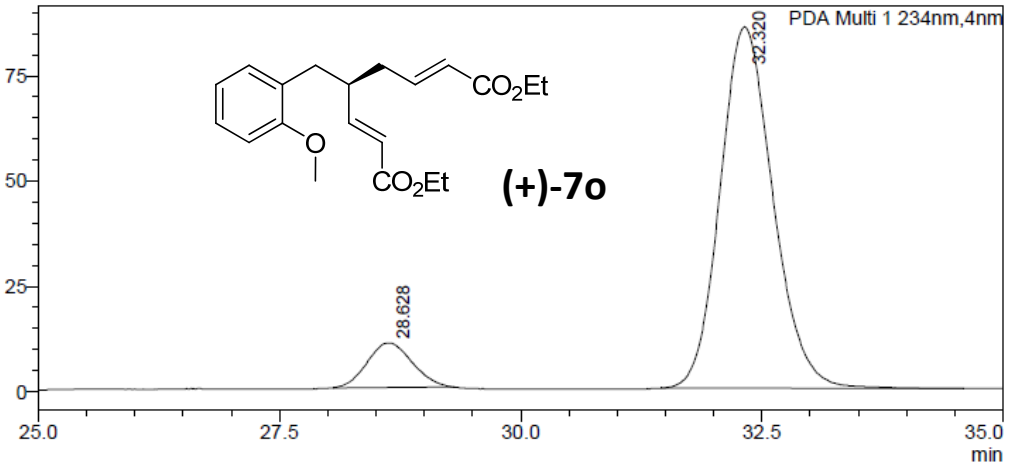
Diasteromeric mixture-7m





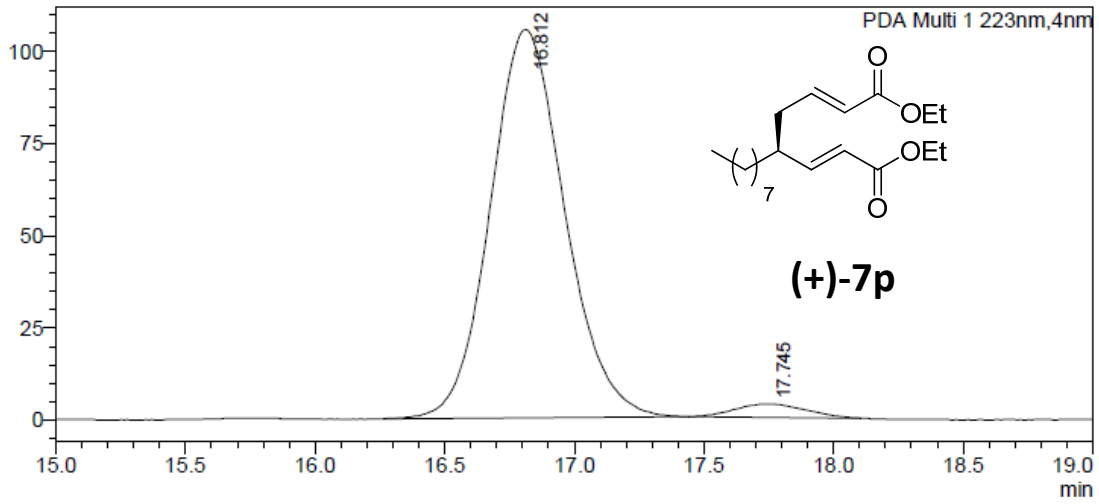
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	10.848	1298	1304	1311	PV 2	24357	340481	0.86%	0.724%
2	10.970	1319	1328	1340	PV	2841474	39624178	100.00%	84.247%
3	12.271	1569	1579	1589	BV	504964	6784036	17.12%	14.424%
4	12.443	1599	1612	1619	VV 5	13314	284368	0.72%	0.605%

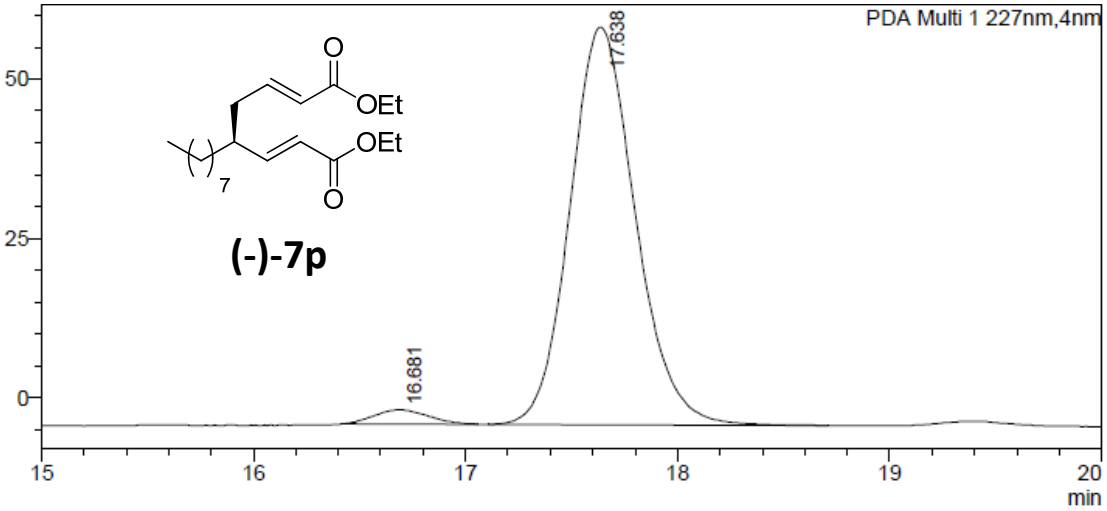




PDA Ch1 234nm

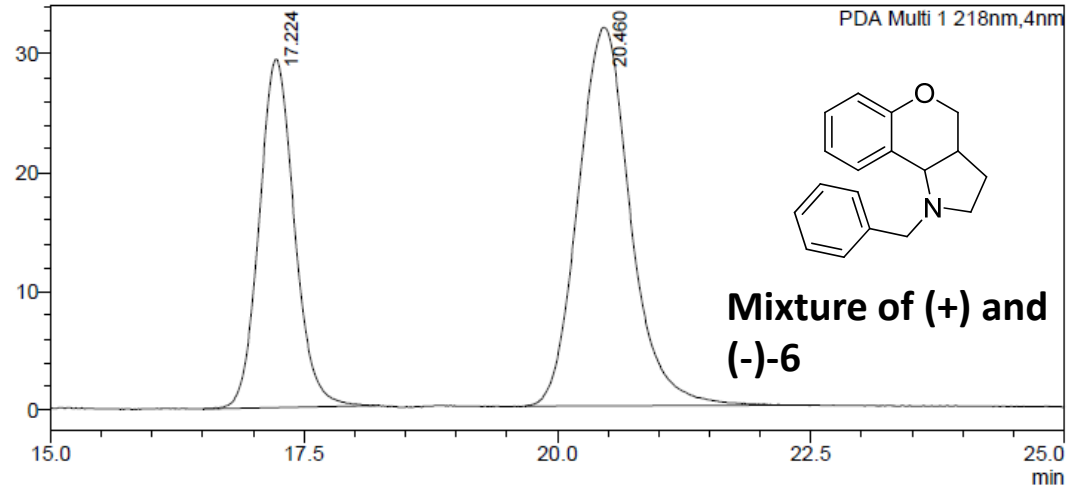
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	28.628	344940	10603	9.532		M	9.532
2	32.320	3273640	85844	90.468		M	90.468
Total		3618580	96447				100.000

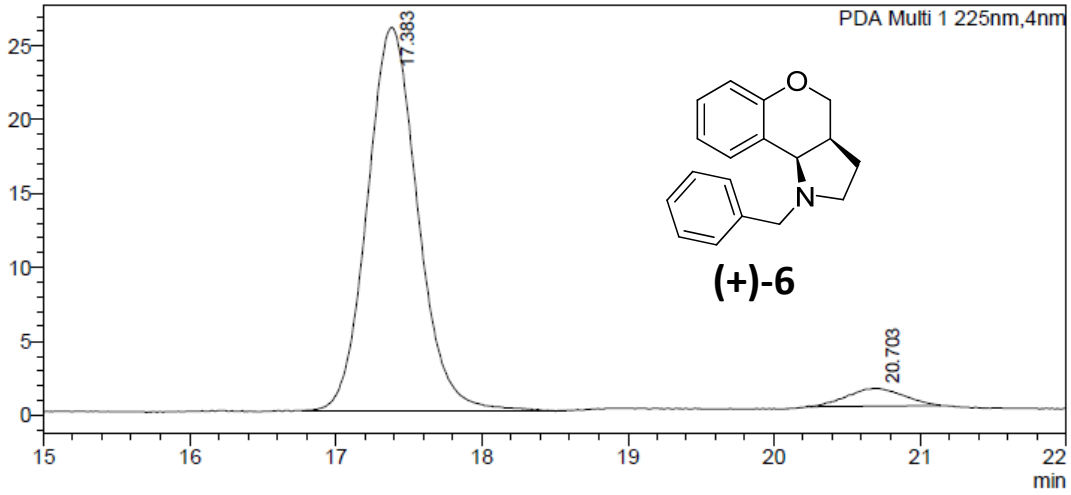




PDA Ch1 227nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	16.681	40077	2242	0.000		M	2.908
2	17.638	1338015	62252	0.000		M	97.092
Total		1378091	64494				100.000





PDA Ch1 225nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Area%
1	17.383	621639	25937	0.000		M	95.034
2	20.703	32483	1197	0.000		M	4.966
Total		654123	27135				100.000